SIMULATIONS AND EXPERIMENTS ON GAS ADSORPTION IN NOVEL MICROPOROUS POLYMERS

A Dissertation in
Materials Science and Engineering
by
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ABSTRACT

Microporous materials represent a fascinating class of materials with a broad range of applications. The work presented here focuses on the use of a novel class of microporous material known as polymers of intrinsic micrioporosity, or PIMs, for use in gas separation and storage technologies. The aim of this research is to develop a detailed understanding of the relationship between the monomeric structure and the adsorptive performance of PIMs. First, a generalizable structure generation technique was developed such that simulation samples of PIM-1 recreated experimental densities, scattering, surface areas, pore size distributions, and adsorption isotherms. After validation, the simulations were applied as virtual experiments on several new PIMs with the intent to screen their capabilities as adsorbent materials and elucidate design principles for linear PIMs. The simulations are useful in understanding the unique properties such as pore size distribution and scattering observed experimentally.
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Chapter 1

Introduction

Microporous materials represent a fascinating class of materials with a broad range of applications. The work presented here focuses on the use of a novel class of microporous material known as polymers of intrinsic microporosity, or PIMs, for use in gas separation and storage technologies. This work is part of an international collaboration involving research groups at the Pennsylvania State University, University of Manchester, and Cardiff University.

The aim of this research is to develop a detailed understanding of the relationship between the monomeric structure and the adsorptive performance of novel microporous polymers known as PIMs. As PIMs were only recently developed, relatively few of the potential polymers have been synthesized and characterization data are lacking. This work began by collecting several experimental adsorption isotherms in the most well characterized and prototypical example, PIM-1. Given a solid basis for comparison, simulations were developed to reproduce experimental data and gain an atomistic understanding of the gas-polymer interaction. Finally, after validating the simulations against experimental data for PIM-1, the simulations were extended to a variety of gases and novel PIMs.

The work presented here resulted in the publication of several papers \(^1-4\). Each chapter of this dissertation is a self-contained document based on each of the publications. Rather than simply placing the publications back to back, the opportunity
was taken to report the results in the most sensible order possible. So while the original publications are maintained as well as possible, data and results from later publications are included with earlier results as relevant.

This chapter aims to orient the reader for sufficient understanding of the rest of the dissertation. The chapter begins with a broad overview of microporous materials, a detailed review of PIMs related research, and then discusses relevant experimental and simulation techniques. While every attempt was made to give a thorough, yet succinct review of the relevant topics, there are, in fact, too many details to cover here. Readers are directed first and foremost to the Handbook of Porous Solids as a foundational reference for further reading on any of the subjects discussed here.

1.1 Microporous Materials

The IUPAC has defined micropores, mesopores, and macropores as pore sizes less than 2 nm, between 2 and 50 nm, and greater than 50 nm respectively. The size ranges are important as they represent differences in physical properties of the materials and their interaction with various fluids. Micropores are similar in size to small gas particles allowing for strong physical interactions between both pore walls and the gas. As a demonstration of the importance of pore width, the potential energy of a gas particle in an ideal slit pore is plotted as a function of distance from the pore center in Figure 1.1. For narrow pores, the gas particle interacts strongly with both walls simultaneously, but as the pore size increases, the adsorbing gas effectively only interacts with one wall or the other.
The following section aims to give a glimpse of the range of porous materials currently in use and under study. As a full, much less a partial, review is beyond the scope of this chapter, the reader is directed to the Handbook of Porous Solids as well as several broadly scoped recent reviews. Given their broad industrial application and research interest as well as their good representation of the diversity of microporous materials, a review of the general architecture and properties of zeolites, metal organic frameworks, and carbonaceous materials is given below.

### 1.1.1 Zeolites

Zeolites represent a unique class of porous material in that they can be found naturally forming as well as synthesized. Zeolites are crystalline aluminosilicate
minerals. Originally used as building materials, zeolites were first recognized, and given their name in 1756 by Axel F. Cronstedt. The first studies into the adsorptive properties of zeolites began in the middle of the 19th century. Natural zeolites, due to their affinity for water vapor adsorption, find practical use in air drying. However, due to impurities in the host rock and their generally lower pore volume, natural zeolites are not as widely used as synthetic zeolites for more specific adsorption and catalysis. Inspired by the naturally occurring zeolites, extensive efforts in creating synthetic zeolites have been undertaken. There are now over a hundred known zeolite structures.

Chemically, most zeolites are almost identical, but they vary widely in pore topology and density. Zeolites are characterized by a cage and window structure with the size of the window being used to classify different zeolites. Careful design of zeolites allows for control of cage and window size making zeolites good as molecular sieves (size selective separations). Given their rigidity and cage and window structure, zeolites are well suited for use as molecular sieves. However, with lower surface areas than activated carbons or MOFs, zeolites are less well suited for gas storage.

1.1.2 Metal Organic Frameworks

The field of organic-inorganic porous frameworks has seen explosive growth over the last several decades. These materials go by any number of names such as hybrid porous solids, metal organic frameworks, isoreticular metal organic frameworks, and porous coordination polymers, among others. These structures consist of a metal ions or polynuclear metal clusters linked by organic ligands via coordination bonds. Like
zeolites, these materials create crystalline structures with well defined pore sizes and shapes. Given the variety of metal centers and organic linkers, not to mention functionalization or post synthetic modification of these linkers, there are nearly infinite possible MOF structures that could be synthesized. This has led to efforts to predict successful structures through classification systems as well as high throughput screening. The fact that the solvent acts as the framework during synthesis, rather than some organic or inorganic template as for zeolites, results in charge neutral frameworks which help to maintain porosity on solvent removal. Even so, thermal stability is one of the main drawbacks of these materials as they typically lose order around 300-400°C. While the pore size can be tuned by judicious choice of linker, large pores allow for multiple interpenetrating networks which can reduce the effective porosity.

Similarly to other microporous materials, MOFs are of interest for separations, gas storage, catalysis, chromatography, sensing, and drug delivery, among other applications. With regards to gas adsorption, MOFs have been created with exceptionally high surface areas and storage capacities. Discrepancies in measured adsorption uptakes have been reported based on synthesis and activation (solvent removal) conditions. For example, high hydrogen loadings of 4.5 wt% at 0.8 bar and 77 K \(^{11}\) have been reported for MOF-5 created at the lab scale, while values of only 1.3 wt% \(^{12}\) have been reported for large scale synthesis. Recently Yaghi and coworkers have reported MOFs with BET surface areas greater than 6000 m\(^2\) g\(^{-1}\) and over 80 mg g\(^{-1}\) of hydrogen uptake (77 K, pressures up to 80 bar) \(^{13}\) demonstrating the great potential and versatility these materials offer in gas separation and storage.
1.1.3 Carbons

1.1.3.1 Activated Carbons

Activated carbons are generally made from an organic material such as wood chips or papermaking byproducts by controlled gasification or carbonization. The first uses of activated carbons date back to the ancient civilizations of Egypt, Greece, and Rome for use medicinally and in water purification. Beginning in the late 1700s, activated carbons were first used on an industrial scale in sugar decolorizing. The use of poison gases in World War I gave rise to the use of activated carbons in gas masks and spurred further research in the area. As the uses for these porous materials grew, research investigated improved understanding and control in their design and manufacture. Perhaps the greatest attribute of these materials, is their adaptability for any given application (powders, monoliths, fibers, fabrics, etc.).

Activated carbons typically contain a wide range of pore sizes, though generally slit shaped in nature. The macro and meso pores allow for fast adsorption and transport of the adsorbate into the porous structure while 90-95% of the surface area comes from the micropores and gives rise to the observed adsorption. Activated carbons, as suggested by TEM and x-ray scattering, consist of a twisted network of carbon layer planes that form into slit shaped microporous structures with some two dimensional, but little to no three dimensional, order. Vacancies or heteroatoms located in the planes, often at the edges, impact the surface chemistry and selective interactions.
1.1.3.2 Specialty Carbons

There exist a wide range of porous carbonaceous materials. Activated carbons have already been discussed, and polymeric materials will be covered next. Between these two broad categories, lies a collection of interesting materials such as carbon aerogels, fullerenes, and nanotubes. By and large, these materials are not widely used in adsorption and separations applications, though not for lack of trying. Most notable in this category are carbon nanotubes. Discovered in 1991, they have undergone intense research for application in numerous fields. Due to the hollow nature of the tubes and the molecule size dimensions, carbon nanotubes were of great interest for gas storage, particularly, hydrogen. Despite initial reports of large adsorption capacities, carbon nanotubes have proven to work no better than other carbonaceous materials.

1.1.3.3 Polymers

Polymers represent an interesting frontier in microporous materials. It is worth noting that meso and macroscopic polymeric materials are also of significant industrial interest, e.g. foams or aerogels. Likewise, polymers are widely used in packaging requiring specific barrier properties to various gases, e.g. oxygen or carbon dioxide. As a microporous material, polymers offer several key advantages, namely designed monomer chemistry, industrial scaling of production, as well as flexibility and physical form. Functionality may be added to a given structure in order to tailor the surface chemistry for specific applications. A wide range of polymers have been produced in large scale, and the infrastructure exists to mass produce polymers. Particularly for membrane
separations applications, the flexibility of polymeric materials is useful. With regards to polymeric materials, this review focuses on hypercrosslinked polymers and polymers of intrinsic microporosity.

Extensive crosslinking of a polymer in a solvent swollen state can create microporosity upon solvent removal in a wide range of polymers\textsuperscript{15}. These hyper-cross-linked polymers, (HCP), can also be made from a reaction that allows the simultaneous formation of the polymer and crosslinks. In contrast to the phase separation induced porosity by nonsolvent porogens in many polymers, hypercrosslinked polymers require thermodynamically compatible solvents to maximize chain swelling, and ultimately microporosity. Experimentally, HCPs have been developed with high surface areas\textsuperscript{16,17} and high hydrogen uptakes of up to 3.68 wt\% (15 bar, 77 K).

The last polymers to be discussed are the recently developed intrinsically microporous polymers. PIMs, which can be insoluble networks or soluble non-networked, derive their porosity from their rigid and contorted monomer structure\textsuperscript{18,19}. Typically, a PIM consists of ladder like fused aromatic ring backbone segments connected by non-linear or non-planar sites of contortion, an example of PIM-1 is given in Figure 1.2. With no stringent chemical criteria, a wide range of PIMs have been proposed and characterization data continues to accumulate\textsuperscript{18}. 


Experimentally, research tends to focus on the synthesis of novel PIM architectures or variations of existing systems. Of particular note is the work of Du and Guiver et al.\textsuperscript{20-23} in which systematic variations in copolymers of PIM-1 are made. Several variations were found to show a degree of tunability in terms of selectivity and permeability of nitrogen and oxygen. The development of networked PIMs such as CTC

Figure 1.2: (a) A single chain of PIM-1 showcasing the rigid backbone segments connected by rigid and nonlinear sites of contortion, here a 1,1-spirobisindane. (b) The prototypical chemical structure of PIM-1.
and Trip-PIM \textsuperscript{25,26} have given rise to some of the largest BET surface areas in PIMs, 830 and 1760 m\textsuperscript{2} g\textsuperscript{-1}, respectively.

Simulation studies have looked to improve the understanding of gas polymer interactions in PIM-1 and other non-networked PIM-1 like polymers \textsuperscript{1,2,4,27-29}. PIMs present many challenges to modeling, starting with the creation of a representative sample. Simulations have thus far focused primarily on characterization, adsorption, and transport properties in PIM-1, though work is expanding to other PIMs.

In attempt to put PIMs in context of other adsorbing materials, Table 1.1 compares the BET surface areas and hydrogen storage capacities of PIMs with hypercrosslinked polymers, activated carbons, and MOFs. Hydrogen is chosen as the basis of comparison here as it is widely measured, not because it is the principal research focus.
PIMs offer a wide range of material structures including both networked and non-networked. Non-networked PIMs offer the advantage of solubility and easy casting of membranes. A quality membrane will have a balance of two competing properties, high permeability and high selectivity. To add further context of PIMs compared to other materials, here in the area of membrane separation, the Robeson plot is reproduced in Figure 1.3.
The aim of this section is to familiarize the reader with the fundamentals of molecular simulations. For a more thorough background, readers are recommended to the works of Frenkel and Smit\textsuperscript{42}, Allen and Tildesley\textsuperscript{43}, and others\textsuperscript{44,45}. Atomistic molecular simulations, based on a detailed knowledge of the positions of each atom,

Figure 1.3: Upper bound correlation for O\textsubscript{2}/N\textsubscript{2} separation, labels for PIM-1 and PIM-7 added in this work. Reprinted from the Journal of Membrane Science, Vol 320, Iss 1-2, Lloyd M. Robeson, The Upper Bound Revisited, Pages 390-400, Copyright 2008, with permission from Elsevier\textsuperscript{41}.
provide a means to observe a microscopically detailed description of physical systems which are often difficult or impossible to discern experimentally. Of particular interest is validating a set of simulations such that they can be applied as virtual experiments to characterize new materials. In the research presented here, two basic types of classical molecular simulations are used, molecular dynamics (MD), and Monte Carlo (MC). Both types of simulations use the same interatomic potential and periodic boundaries, but differ with regards to how they explore phase space and reach equilibrium configurations from which data are collected.

For both MC and MD simulations the same force field is used to describe interparticle interactions. Force fields differ from one another in both functional form and the means by which parameters are obtained. In classical molecular simulations each atom, or group of atoms, are represented as a single particle with a particular size, interaction energy parameter, and charge. The total potential energy of the systems in this work is calculated by:

\[
E_{\text{pair}} = \sum_{\text{bonds}} k_r (r - r_{eq})^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_{eq})^2
\]

\[
+ \sum_{\text{dihedrals}} \frac{v_n}{2} \times [1 + \cos(n\phi + \gamma)] + \sum_{i < j} 4\varepsilon_{ij} \left( \frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}} \right) + \frac{q_i q_j}{k \varepsilon r_{ij}} \tag{1.1}
\]

Bond lengths and angles are defined according to a harmonic potential where the deviation of the current bond length, \( r \), or angle, \( \theta \), from equilibrium (\( r_{eq} \) or \( \theta_{eq} \)) is squared and multiplied by a force constant, \( k \). Dihedrals follow the cosine series where \( n \) is the multiplicity, \( \phi \) is the current angle, \( \gamma \) is the phase shift or equilibrium angle, and \( v_n \) is the barrier height.
Nonbonded interactions are comprised of van der Waals interactions and Coulombic interactions in the last term of Eq. 1.1, and depend on the distance \( r_{ij} \) between particles \( i \) and \( j \). The Lennard-Jones (LJ) potential is a widely used mathematically simple model that describes the van der Waals interaction between two particles. The LJ potential requires two parameters, the well depth \( \varepsilon \), and the collision diameter \( \sigma \). Different force fields fit these parameters to reproduce various data, from experiments or other simulations. Due to the time consuming and difficult process of parameter determination, parameters for interactions between different particle types are typically calculated by mixing pure component parameters. In this work, Lorentz-Berthelot mixing rules are used, in which an arithmetic mean of \( \sigma \) and a geometric mean of \( \varepsilon \) are taken:

\[
\begin{align*}
\sigma_{ij} &= \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) \\
\varepsilon_{ij} &= \sqrt{\varepsilon_{ii} \varepsilon_{jj}}
\end{align*}
\]  

(1.2)

While Lorentz-Berthelot mixing can overestimate the well depth, they are widely and successfully applied. In Figure 1.4, the LJ potential is plotted along with the attractive and repulsive components. The LJ potential well depth is determined by \( \varepsilon \), while the position of the minimum is at \( 2^{1/6} \sigma \). The \( (\sigma/r)^{12} \) term represents the repulsion caused by the hard core overlap of electron orbitals while the \( -(\sigma/r)^{6} \) term represents the attraction from London dispersion forces.
The simulations used in this work aim to measure bulk material properties, thus periodic boundary conditions are employed in all three dimensions. Periodic boundaries allow the simulation to consider a single representative sample of the material from within the bulk. Each repeated cell is called a periodic image, and as a particle passes from the original cell to the next, the particle from a periodic image passes back into the original image. An example of a periodic image is given in Figure 1.5. Particles are prohibited from interacting with their own periodic image by the minimum image convention, this entails the cutting off of long range interactions at a predefined distance less than or equal to half the box length. For short range van der Waals interactions, that fall off like $1/r^6$ or faster, the potential energy goes to zero quickly enough that even at

![Figure 1.4: The Lennard-Jones potential (--) and the individual contributions from the attractive dispersion (- -) forces and repulsive electron orbital overlap ( • •). The LJ potential has a well depth of $\epsilon$ located at $2^{1/6}\sigma$.](image-url)
small cubic box sizes of side length 30 Å, the minimum image convention can be applied without issue. However for electrostatic interactions, which fall off like $1/r$, prohibitively large samples would be required for the potential energy to approach zero, thus Ewald sums $^{46}$ are used to account for long range electrostatic interactions. Without periodic images, the majority of particles in any simulation of manageable size would be near enough the edge to be influenced by surface effects. Care must be taken to create a periodic box that is large enough so as to avoid artifacts (for example phonons or wavelengths are limited by the box size), but also small enough to allow the simulations to run in a reasonable amount of time.
In this work, a pseudo atomistic description of the systems is used. While molecular simulations are powerful, the calculation of interparticle interactions are expensive and eventually define a limit in the size of the system one can simulate. In order to reduce the number of particles in the system, one can employ coarse graining, in which a single sphere is used to represent multiple atoms. The so called united atom (UA) model is the limiting case in which only hydrogen atoms are coarse grained out of the system. Its use is justified in many cases, the present simulation of PIMs included, in which specific interactions with hydrogen atoms are not expected to play an important role.

Figure 1.5: A simulation sample is shown in red, with its periodic images shown surrounding it. As a particle moves out of the sample, the particle from the periodic image moves back into the sample (see arrows). This allows the simulation of bulk material properties with only a small sample. To avoid interactions between self-images, a cut off distance, $r_c$, is used beyond which all van der Waals interactions are set to zero.
role. UA parameters in this work are taken from the transferable potential for phase equilibria \(^ {47}\) (TraPPE), and as the TraPPE forcefield developers suggest, bonded interactions are taken from the generalized AMBER forcefield (GAFF) \(^ {48}\). The GAFF was developed specifically for proteins and organic molecules making it well suited for use with polymers. The GAFF balances simple interatomic potentials with relatively few atom types covering a broad range of chemical space for organic molecules. Where specific parameters have not been defined, they can be estimated according to empirical formulas. The GAFF performs as well or better to Tripos 5.2, MMFF94, CHARMM, and PARM99 in crystallographic structure minimization, gas phase modeling of nucleic acid base pairs, and relative energies of conformational pairs \(^ {48}\).

### 1.2.1 Monte Carlo Simulations

Monte Carlo simulations are a stochastic simulation technique in which the dynamics of particles are generally ignored. The simulations move from an initial configuration, through phase space, towards some minimum energy equilibrium configuration by a series of steps. The name Monte Carlo was chosen due to the central importance of random numbers and sampling. At each step of the simulation, a random number is generated to determine the move type to attempt, another random number is generated to determine the atom or group of atoms on which the move will be attempted, random numbers are used to determine the magnitude of the move, and if an increase in energy is produced, a random number is used to judge its acceptance. The only requirement of MC moves is that the system progresses towards equilibrium; in general
there is no need for the moves to be physically realistic. After a move is attempted, the change in the system energy is evaluated. If the energy decreases, the move is accepted automatically. If the energy increases, the move is accepted according to the Boltzmann distribution, that is, if the energy increases, the move is accepted with decreased probability as if it were caused by thermal fluctuations according to Eq. 1.3:

$$\text{acc}(o \rightarrow n) = \min(1, \exp\{-\beta[U(r'^N) - U(r^N)]\})$$

(1.3)

Where $o$ and $n$ are the old and new states respectively, $\beta$ is $1/k_B T$, $U$ is the potential energy for the particular configuration, $r'^N$, of the $N$ particles.

When using molecular simulations, one must consider the ensemble, or set of conditions under which to work. Adsorption is a phenomenon suited to modeling by the so called Grand Canonical (GCMC) ensemble, where the chemical potential, volume and temperature of the system are held fixed and the pressure and number of particles is allowed to fluctuate. In GCMC simulations, particles are exchanged between the simulation sample and a fictional reservoir or particle source that is in an ideal state. Through an equation of state, the pressure can be related to the chemical potential such that by specifying the temperature and chemical potential of the reservoir, one may specify the chemical potential and temperature of the adsorbed phase. After the system equilibrates, the number of particles adsorbed is averaged.

Of the wide range of MC moves that could be employed, this work utilizes only simple insertions/deletions, translations, and rotations of the gas particles. Insight into polymer dynamics during adsorption are of interest, however, MC moves are not well suited to modeling the motion of PIMs. Given the highly interconnected nature of the
atoms in the fused aromatic ring structures of PIM monomers (see Figure 1.2), any individual movement of atoms will result in large changes in energy and vanishingly small acceptance probabilities. Even highly coordinated movements of chain segments are nearly impossible at experimentally realistic densities. Thus, the polymer is considered fixed and rigid during adsorption and all polymer motions are only considered in MD simulations.

1.2.2 Molecular Dynamics

In much the same way that MC is not suited to the simulation of PIM dynamics but is well suited to adsorption, MD is well suited to PIM dynamics, but not adsorption. In this work, MD simulations are used to compress and relax the initial structures into well relaxed systems of realistic density. In MD simulations, particles are assumed to follow classical mechanics such that, given the initial positions and momenta of each particle, the subsequent configuration of the system may be calculated by Newton’s equations of motion.

In a manner analogous to experiments, the simulation sample must first be prepared, then the MD simulation is run until equilibrium is reached, and finally, the quantities of interest are measured over some period of time. Given the initial coordinates of all the particles in the simulation, a non-trivial task for PIMs as described in later chapters, velocities are assigned according to the Boltzmann distribution at the desired temperature. The force on each particle can be calculated from the potential energy by Eq. 1.4:
\[ F_i(r_1, r_2, ..., r_N) = -\nabla_{r_i} U(r_1, r_2, ..., r_N) \] (1.4)

Which, combined with an efficient integration technique, here the velocity Verlet algorithm, allows for the fast computation of the positions and velocities for each subsequent time step (Eq. 1.5):

\[
\begin{align*}
    r(t + \Delta t) &= r(t) + v(t)\Delta t + \frac{F(t)}{2m} \Delta t^2 \\
    v(t + \Delta t) &= v(t) + \frac{F(t + \Delta t) + F(t)}{2m} \Delta t
\end{align*}
\] (1.5)

While further details and in depth discussion of MD simulations is beyond the scope of this work, it should be noted that simulations were run with the Nosé-Hoover thermostat \(^{49, 50}\) and barostat \(^{51}\) in the NVT and NPT ensembles.

### 1.3 Characterization

In this section, relevant characterization techniques will be briefly reviewed. An overview of surface area, pore size distribution, scattering, and adsorption measurements by both simulations and experiments will be discussed. The IUPAC has stated that no experimental method, however elegant it might be, is capable of yielding absolute values of surface area, pore size etc. As a consequence, we should not always expect to obtain perfect agreement between the corresponding parameters (e.g., the pore size distribution obtained from say, nitrogen adsorption and PALS).
1.3.1 Surface Area

The surface area (SA) of a material is often measured and reported with great enthusiasm. However, these reports must be read and interpreted with caution. The surface area is frequently used as a proxy for adsorption sites, and indeed linear relationships between surface area and amount adsorbed have been found for many materials. The two most common values reported are the Langmuir and Brunauer-Emmett-Teller, or BET, surface areas, and it is important to realize these are not necessarily the true surface areas (such as could be calculated from a well-defined unit cell of a crystalline material).

In the Langmuir model, the adsorbent material is considered to have active adsorption sites to which only a single adsorbate adsorbs, all adsorbed molecules do not interact, nor do they form multiple layers. The BET method extends the Langmuir theory to multilayer adsorption by allowing an already adsorbed molecule to act as an adsorption site for the adsorption of molecules in the next layer. Following from the kinetic derivation of the Langmuir model in which equilibrium is defined as the rate of adsorption being equal to the rate of desorption, the BET model extends this between layers as:

\[ a_i p \theta_i \theta_{i-1} = b_i \theta_i e^{E_i/RT} \]  \hspace{1cm} (1.6)

where \( a_i \) and \( b_i \) are the adsorption and desorption constants, \( \theta \) is the fraction of the surface covered in each layer \( i \), and \( E_i \) is the energy of adsorption at pressure \( p \). In principle, each layer can have different values, but it is generally assumed that beyond the first layer all constants are equal, with \( E_i \) taken as the liquefaction energy. This implies no lateral
interactions between adsorbed particles and uniform sites of adsorption. Further
assuming that at partial pressure $p/p_0 = 1$ the multilayer has an infinite thickness, the
standard form of the BET equation $^{53}$ is derived as Eq. 1.7 where $n_m$ is the monolayer
capacity:

$$\frac{p/p_0}{n(1 - p/p_0)} = \frac{1}{n_mC} + \frac{C - 1}{n_mC} \left( \frac{p}{p_0} \right)$$  \hspace{1cm} (1.7)

Experimentally, one can measure many different surface areas, the same is true in
simulations. The most commonly considered surface areas are the accessible and
Connolly surface areas, shown in Figure 1.6. The Connolly surface is defined by the
bottom edge of a probe molecule rolling over the surface of the material, whereas the
accessible surface is defined by the middle of a molecule rolling over the surface. It has
been suggested that the accessible surface area provides a better comparison to the
commonly reported BET areas $^{54}$. 
The detailed knowledge of atomic positions allows the direct calculation of the surface area by Monte Carlo integration, even for amorphous materials. A test probe is placed such that it touches a random point on the surface of particle \( i \) in the simulation, overlap between the probe and other framework atom is tested, and the fraction of non-overlapping probes is the fraction of particle \( i \)’s surface area that contributes to the total surface area summed over all particles \( i = 1, 2, \ldots n \).

1.3.2 Pore Size Distribution

The pore size distribution (PSD) is an important material characteristic. As indicated by the IUPAC pore size naming scheme (micro-, meso-, and macro- pores), the

Figure 1.6: The accessible (-) and Connolly (-- -) surfaces are visually defined and compared. Grey spheres represent framework atoms while open spheres are the test probe.
interaction between the solid adsorbent and the adsorbate is strongly influenced by pore size (see Figure 1.1). There are several methods by which one can calculate the PSD, by both experiments and simulations. Experimentally, two common methods are the Horvath-Kawazoe method and Positron Annihilation Lifetime Spectroscopy. From simulations, there are several approaches, one a MC integration and the other a geometric calculation.

1.3.2.1 Positron Annihilation Lifetime Spectroscopy

Positron Annihilation Lifetime Spectroscopy (PALS) relates the size of a pore to the lifetime of a positron, an antiparticle with a mass of an electron and a positive charge. There are two types of positronium, bound positron electron pairs, \textit{para}, which has an extremely short 125 ps lifetime and \textit{ortho}, which has a longer 142 ns lifetime in vacuum. In insulating materials, positrons preferentially locate in electron poor regions, that is, pores. Trapped in a pore, the positron will interact with a molecularly bound electron and convert to the \textit{para} state, quickly annihilating \textsuperscript{5}.

For small pores, radius less than 2 nm, the Tao-Eldrup model gives a good relation between lifetime and pore size, while larger pore sizes up to 30 nm require more recently developed theory. The Tao-Eldrup model assumes the positron is localized in an infinitely deep well and only undergoes pickoff annihilation when it is sufficiently close to the pore wall. Several open software packages can be used to analyze experimental spectra and create PSDs given several assumptions about pore geometry and fitting the decay to a continuum of lifetimes. This fitting to a continuum of lifetimes creates non
unique solutions. The situation becomes further complicated for percolated and tortuous pore structures.

### 1.3.2.2 Horvath-Kawazoe Method

Perhaps due to the widespread popularity of the BET surface area, the Horvath-Kawazoe (HK) method of pore size determination is commonly reported. Like the BET surface area calculation, the HK method relates the PSD to low temperature nitrogen adsorption. This model is based on the assumption that the pressure at which a pore fills is directly related to the adsorbent-adsorbate interaction energy. It is assumed that with respect to pore size, the change in energy on adsorption is much greater than the change in entropy.

Originally, this method was derived for nitrogen in a carbonaceous material with slit pores, but it has since been expanded to other materials, gases, and pore geometries. For nitrogen in molecular sieve carbons at 77 K, the equation relating pressure to pore width for nitrogen adsorbing into a carbon is given as Eq. 1.8

$$\ln\left(\frac{p}{p_0}\right) = \frac{61.23}{(H - 0.64)} \left[ \frac{1.895 \times 10^{-3}}{(H - 0.32)^3} - \frac{2.709 \times 10^{-7}}{(H - 0.32)^9} - 0.05014 \right] \tag{1.8}$$

where $p_0$ is the saturation pressure, and $H$ is the pore width in nanometers. The many empirical parameters relate to the size of the adsorbent and probe atoms. Interaction potential and parameter modifications would be needed for other gases and non-carbon, non-homogeneous surfaces, nevertheless, it is used as is, with some frequency. Given Eq. 1.8, one needs a relative pressure of $10^{-7}$ to see pores of 0.4 nm, such low pressures
are difficult to achieve experimentally. When ultramicropores, which fill at pressures below those experimentally achievable, are present, their contribution is combined with the smallest visible pore size $^{18}$.

1.3.2.3 Simulations

In simulations, the PSD can be calculated geometrically or by MC integration. In both cases, the simulations measure the fractional free volume (FFV) available to a probe of a given size. The FFV function is a monotonically decreasing function of probe size, the derivative of which gives the PSD or change in volume with change in pore size. The MC integration technique is described well by Gelb and Gubbins $^{57}$. A point is randomly selected in the sample, outside of the framework atoms. The simulation proceeds to find the largest sphere that can both contain that point and not overlap with nearby framework atoms. This produces the FFV curve which can be differentiated to obtain the PSD.

The geometric calculation starts by overlaying a fine mesh of points throughout the simulation sample. Points can be marked as occupied or unoccupied by the framework. The largest test probe that can be placed at each point without overlapping with the framework is found. This gives the FFV as a function of probe size, which is differentiated to get the PSD $^{58}$. The advantage to this technique is that given a sufficiently fine grid, the pore volume can be estimated.
1.3.3 X-Ray Scattering

Calculation of the structure factor from simulation samples is a well established practice. The scattering data are calculated from partial radial distribution functions by Eq. 1.9:

\[ I(q) = \langle \rho \rangle \int dr \, 4\pi r^2 \frac{\sin qr}{qr} \sum_{a,b} f_a x_a f_b x_b [g_{ab}(r) - 1] \] (1.9)

where \( I(q) \) is the scattering intensity as a function of wave vector \( q \), \( \rho \) is the average number density of the system, \( g_{ab} \) is the partial radial distribution function of atomic species \( a \) and \( b \), \( f \) is the scattering length and \( x \) is the mole fraction of each species in the system. As this work uses a UA model, a first approximation of the scattering pattern was calculated ignoring contributions from hydrogen. This approximation is justified by both the small scattering length of hydrogen and the small mole fraction of hydrogen in all PIMs studied here.

1.4 Bibliography


Chapter 2
Experimental CO$_2$ and CH$_4$ Adsorption in PIM-1

2.1 Introduction

A wide range of adsorbent materials are currently in use for applications in gas storage and separations. In particular, CO$_2$ and CH$_4$ adsorption based separations are of interest due to the greenhouse effect of these gases when released to the atmosphere. Materials that have been assessed include aluminosilicates, aluminophosphates, activated alumina, activated carbons, pillared clays, silica gels, metal organic frameworks (MOFs), hypercrosslinked polymers and polymers of intrinsic microporosity (PIMs). An ideal material will have a combination of micropores, to provide high surface areas, and macropores for fast sorption kinetics. Micropores are those with diameter less than 2 nm, generally of a size equivalent to a few molecular diameters of the adsorbed gas, as defined by the IUPAC. Mesopores are between 2 and 50 nm while macropores are larger than 50 nm.

Comprehensive reviews have been recently published on the state of the science on porous materials for CO$_2$ separations. Despite the intense research that has focused on MOFs, PIMs, even with potentially smaller capacities, offer an interesting alternative in that they are not expected to be as sensitive to water. Recently much attention has been given to the development of microporous polymers that can selectively adsorb carbon dioxide.
Most polymers, due to their highly flexible backbones, pack together into dense, and often crystalline systems, and until recently have not been considered as adsorbents for gas storage. According to Germain et al.\textsuperscript{20} porous polymers are generally less sensitive to air while compared to MOFs. Additionally, they are made of organic components with a wide range of synthesis routes, easy to handle and mechanically robust.

High surface area polymers can be created by several methods. One technique involves crosslinking polymers that include porogens, or inert solvent molecules, during the polymerization to create polymers with surface areas up to 1000 m\textsuperscript{2}/g. Alternatively, a polymer precursor can be swollen in a thermodynamically good solvent to induce chain separations and subsequently be crosslinked to produce the so called hypercrosslinked polymers. By rapidly creating many crosslinks, the polymer chains are locked in place and porosity remains after solvent removal.\textsuperscript{21} Hypercrosslinked polymers utilize rigid crosslinks to prevent the system from condensing into a nonporous state. Lee et al.\textsuperscript{22} report H\textsubscript{2} storage capacities of 3.04 wt % at 77 K and 15 bar, and the same group\textsuperscript{23} reported 5.2 mmol/g of CH\textsubscript{4} at 298 K and 20 bar.

Different from crosslinking, polymers of intrinsic microporosity (PIMs)\textsuperscript{5} rely on backbones that lack sufficient flexibility and linearity to pack space efficiently. The prototypical example of this class of polymers is PIM-1 (see Figure 2.1) which has a rigid backbone that consists of fused aromatic rings and a spirobisindane that acts as a contortion site to remove planarity. PIMs have been developed with surface areas from 700 to 1000 m\textsuperscript{2}/g and hydrogen uptakes as high as 1.7 wt% at 0.1 MPa and 77 K.\textsuperscript{5}
triptycene based PIM capable of taking up 2.7 wt% of H\textsubscript{2} at 77 K and 10 bar\textsuperscript{24} has also been developed.

Figure 2.1: (a) Chemical structure of PIM-1 and (b) molecular model of a single chain of PIM-1 showing the rigid and contorted structure.

Porous polymers offer many potential advantages over other microporous adsorbents. The composition of polymers is primarily of lightweight elements, which is particularly important for weight critical applications such as transportation. There is also the potential to process porous polymers at the industrial scale. Finally, there exist a
wide variety of chemistries for porous polymers and chemical modifications allowing the material to be tailored to specific applications.

Here experimental data of CO$_2$ and CH$_4$ adsorption in PIM-1 at several temperatures are presented. Enthalpies of adsorption and selectivities are calculated from the isotherms. Kinetic analysis accounting for both Fickian diffusion and polymer relaxation gives diffusion coefficients and relaxation times.

### 2.2 Theory and Models

#### 2.2.1 Adsorption Equilibria

Adsorption isotherms were correlated to known models to calculate the energetics of adsorption and predict the selectivity of the material towards carbon dioxide. Isotherms can be fitted to a second order virial adsorption isotherm of the form:

$$ HP = n \exp(C_1 n + C_2 n^2) $$

where $H$ is Henry’s constant, $P$ is the pressure, $n$ is the amount adsorbed, and $C_1$ and $C_2$ are the adsorption virial constants. The virial equation is one of the most flexible isotherm models capable of correlating a wide variety of isotherms; nevertheless, it does not provide much physical insight as to the nature of the process taking place.

Other models, like the Langmuir isotherm, provide some insight into the physics of the system but are often limited in their applicability to selected cases. The dual mode (DM) isotherm, proposed by Barrer et al.\textsuperscript{25} to describe adsorption in glassy polymers, is a simple model that has been widely used to correlate adsorption of gases in polymers. The
model assumes that there is a porous component of the material that behaves according to the Langmuir model, and there is a liquid-like fraction of the material that can dissolve gases according to Henry’s law. The DM model gives the amount adsorbed as:

\[ n = m \frac{K_1 P}{1 + K_1 P} + K_2 P \]  \hspace{1cm} (2.2)

where \( n \) is the amount adsorbed, \( m \) is the saturation capacity of the porous component, \( K_1 \) is the Langmuir affinity constant, and \( K_2 \) is the Henry’s constant that describes the molecular dissolution in the polymer. At high pressures, the activity of the gas is better described by the fugacity and Eq. 2.2 can be rewritten as:

\[ n = m \frac{K_1 P \phi}{1 + K_1 P \phi} + K_2 P \phi \]  \hspace{1cm} (2.3)

where \( \phi \) is the fugacity coefficient.

Isotherms at three different temperatures were measured for each gas to allow the determination of enthalpies of adsorption, \( \Delta H \). The enthalpy of adsorption characterizes the strength of interaction between the adsorbent and adsorbate. The enthalpy of adsorption is calculated by the Clausius-Clapeyron equation as the slope of the logarithm of the pressure versus the inverse temperature, \( T \), at constant loading:

\[ \frac{\Delta H}{R} = \left( \frac{d \ln P}{d \left(1/T\right)} \right)_{\text{m}} \]  \hspace{1cm} (2.4)

where \( R \) is the universal gas constant. Accurate temperature control is one of the most important factors that ensure small errors in the determination of the enthalpies of adsorption. In this work, variations in the temperature during measurements were less than 0.1 K.
Prediction of mixture selectivity from pure component isotherms may be inaccurate if the system presents strong deviations from the model used, nevertheless, it is a valuable tool to estimate the performance of a given material. The selectivity towards a component in a mixture is defined as:

\[ s_{1,2} = \frac{x_1/y_1}{x_2/y_2} \]

(2.5)

Mixture selectivity can be calculated from the DM model mentioned before. Alternatively, a model like the Ideal Adsorbed Solution Theory (IAST)\(^\text{26}\) that does not make any assumption on the adsorption mechanism can also be used. It should be noted that both models have their own limitations. In both models, it is assumed that there is no interaction between adsorbed species. The DM model has the additional assumptions that there is a fixed region that behaves according to the Langmuir model (constant number of sites, one molecule per site, all sites are indistinguishable, etc.) and a region where the polymer behaves as a liquid. On the other hand, IAST assumes that the solid is rigid. Evidently both of these models are approximations and the aim in this work is to understand the difference in the predictions of both models. Although other models exist to describe sorption of mixtures in polymers\(^\text{27, 28}\), the results are similar to the DM model and will not be analyzed.

The amount adsorbed of component \(i\) from a gas mixture using the DM model is given by:

\[ n_i = \frac{m_i K_{1i} P y_i}{1 + \sum_i K_{1i} P y_i} + K_2 P y_i \]

(2.6)
where \( y_i \) is the gas phase mole fraction. As mentioned before, at high pressures, a fugacity coefficient should be included to account for the non-ideality of the gas mixture:

\[
n_i = \frac{m_i K_{ji} P y_i \bar{\phi}_i}{1 + \sum_j K_{ji} P y_j \bar{\phi}_j} + K_{ji} P y_i \bar{\phi}_i
\]  

(2.7)

where \( \bar{\phi}_i \) is the fugacity coefficient of component \( i \) in the mixture, \( m_i \) is the pure component saturation capacity of the Langmuir contribution to the isotherm, and \( K_{ji} \) are the constants for pure component \( i \) as described by Eq. 2.6. Thermodynamic consistency requires all values of \( m_i \) to be the same, which is not often the case, and a practical approximation is to use individual values of \( m_i \) obtained from pure component isotherms.

Adsorption equilibria can also be predicted using the IAST. For a binary mixture, the following set of equations needs to be solved:

\[
PY_1 \bar{\phi}_1 = p^*_1 x_1
\]  

(2.8)

\[
PY_2 \bar{\phi}_2 = p^*_2 x_2
\]  

(2.9)

\[
\int_0^{p_1^*} n_1^*(f) dlnf = \int_0^{p_2^*} n_2^*(f) dlnf
\]  

(2.10)

\[
\frac{1}{n} = \frac{x_1}{n_1^*} + \frac{x_2}{n_2^*}
\]  

(2.11)

where \( x_i \) is the adsorbed phase composition, \( y_i \) is the gas phase composition, \( p^*_i \) is the standard pressure of component \( i \) at the spreading pressure of the mixture, \( n_i^* \) is the amount adsorbed of the pure component \( i \) at the spreading pressure of the mixture, and \( \bar{\phi}_i \) is the fugacity coefficient of component \( i \) in the mixture that can be determined from an equation of state. \( n_i^*(f) \) is the pure component isotherm with the pressure (or fugacity) as independent variable. When the amount adsorbed is the independent variable in the adsorption isotherm model, then Eq. 2.10 can be written as:
The selectivity at zero coverage calculated from Eq. 2.8 - 2.11 using the virial equation (Eq. 2.1) or the Langmuir model is simply the ratio of the Henry’s constants:

\[
\frac{s_{1,2}}{x_1/y_1} = \frac{H_1}{H_2}
\]  

In many cases, there is no analytical solution for the selectivity and the system of equations has to be solved numerically. Typically, the temperature, pressure and gas phase compositions are specified, and the amount adsorbed and adsorbed phase compositions are calculated. Therefore, it is possible to obtain the selectivity as a function of pressure at each temperature.

### 2.2.2 Adsorption Kinetics

The adsorption process of a gas into a polymer is complex, and a more complete understanding can be obtained by looking at the adsorption kinetics. At short time scales, adsorption is diffusion limited with the kinetics following ideal Fickian adsorption where the uptake is proportional to the square root of time. At longer time scales, adsorption is controlled by the relaxation of the polymer. If the diffusion coefficient is sufficiently high and the relaxation times sufficiently long, the two processes can be separated and complex data modeled in such a way as to derive information regarding the diffusion coefficient as well as polymer relaxation times. Following the work of Berens and Hopfenberg, the kinetic
adsorption data was modeled as a linear superposition of an ideal Fickian, and a relaxation controlled contribution:

\[ M_t = M_{t,F} + M_{t,R} \]  \hspace{1cm} (2.14)

where \( M_t \) is the fractional mass adsorbed at time \( t \), \( M_{t,F} \) and \( M_{t,R} \) are the contributions of the Fickian and relaxation processes at time \( t \), respectively.

The gas uptake in a purely Fickian process for a spherical particle is \(^{30}\):

\[ M_{t,F} = M_{\infty,F} \left[ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{4Dn^2\pi^2 t}{d^2} \right) \right] \]  \hspace{1cm} (2.15)

where \( M_{\infty,F} \) is the equilibrium mass adsorbed in a Fickian process, \( D \) is the diffusion coefficient, and \( d \) is the particle diameter. When the particle has an initial loading, Eq. 2.15 needs to be modified. As polymers are described as having a distribution of relaxation times, the relaxation controlled adsorption process becomes a sum of the contribution from adsorption due to each characteristic relaxation time \(^{29}\):

\[ M_{t,R} = \sum_{i} M_{R_i} \left[ 1 - \exp(-t/\tau_i) \right] \]  \hspace{1cm} (2.16)

where \( M_{R_i} \) is the equilibrium mass adsorbed of the \( i \)th relaxation process and \( \tau_i \) is the characteristic time for relaxation of the \( i \)th mode. As the number of fitting parameters increases by two for each additional characteristic relaxation time, it is recommended to use the lowest number of relaxation times that provide a good representation of the experimental data. In the present work, a single relaxation time accurately describes the observed adsorption behavior.
2.3 Experimental Procedure

2.3.1 Materials

In this study, PIM-1 was prepared following previously published procedures\textsuperscript{31} to produce a bright yellow powder. The sample was observed to have a wide range of particle sizes, estimated from 50-200 μm via optical microscopy. The same sample was used for all isotherms. Gases were used as supplied by the manufacturer (BOC Gases): helium grade 5.0 (99.999 %), carbon dioxide grade 4.5 (99.995 %), and methane grade 2.5 (99.5 %).

2.3.2 Methodology

Measurements were performed using an IGA-001 from Hiden Isochema, equipped with a vacuum pump (vacuum pressure <10^{-6} bar), a water thermostat bath and a gas supply. A sample of 66.731 mg was loaded into the glass sample holder. The sample was heated at a rate of 2 K/min from room temperature up to 393 K using an electric furnace, and maintained between 380 K and 400 K for 8 hours in order to thoroughly outgas the sample. A total mass loss of 2.763 mg was observed (4.1%).

The density was determined by measuring the buoyancy of the sample in an inert gas, helium. The sample was cooled to 310 K and the weight measured over a range of pressures up to 20 bar. We assume that the interaction between the polymer and the helium is negligible compared with the amount of helium displaced by the polymer. The density was measured as 0.94 g/cm\textsuperscript{3}. We assume that the density of PIM-1 is
independent of the temperature over the temperature range of our experiments, and use the density measured at 310 K for buoyancy correction in all isotherms.

Adsorption and desorption isotherms were measured following standard procedures. The sample temperature was set and maintained via a water bath to ensure minimal temperature fluctuations. Typical temperature fluctuations during a single measurement were less than 0.1 K, while baseline drifts over the 48 hours that was required to collect the whole isotherm were less than 0.5 K. Gas is injected into the sample chamber until the desired pressure is reached. The system then maintains the desired pressure and monitors the sample weight. After either the weight fluctuations have reached a desired level or after a specified amount of time has elapsed, the sample weight is recorded and the next pressure step commences. Due to the plastic nature of polymers, equilibration times can be prohibitively long, thus the sample mass after between 60 and 180 minutes is taken as the pseudo-equilibrium mass, following the protocol used by Visser and Wessling. 32

2.4 Results and Discussions

Experimentally measured sorption isotherms for CO$_2$ and CH$_4$ in PIM-1 at three different temperatures are shown in Figure 2.2 with fits from the Virial equation (Eq. 2.1) and the dual mode model (Eq. 2.2). The parameters for the correlations are summarized in Table 2.1 and 2.2. Figure 2.2 shows small differences between the two models, but both of them correlate well the experimental data.
Figure 2.2: Sorption isotherms of CH$_4$ and CO$_2$ in PIM-1, open symbols represent adsorption, closed symbols desorption, solid lines are correlations from the dual mode model and dashed lines are correlations using the virial model. The individual isotherms have the following nomenclature: adsorption of CO$_2$ at 20.3°C (○), desorption of CO$_2$ at 20.2°C (●), adsorption of CO$_2$ at 36.4°C (□), desorption of CO$_2$ at 36.4°C (■), adsorption of CO$_2$ at 53.4°C (Δ), desorption of CO$_2$ at 53.6°C (▲), adsorption of CH$_4$ at 20.0°C (○), desorption of CH$_4$ at 19.9°C (●), adsorption of CH$_4$ at 36.8°C (∗), desorption of CH$_4$ at 36.8°C (×), adsorption of CH$_4$ at 54.3°C (+), and desorption of CH$_4$ at 54.2°C (–).
It is clear from the isotherms that a saturation capacity has not been reached even at 20 bar and the lowest temperature used in the experiments. The highest capacities measured were 6.07, 4.95, and 4.05 mmol/g of CO$_2$ at 20.3, 36.4, and 53.5°C respectively and 2.52, 2.10, and 1.69 mmol/g of CH$_4$ at 20.0, 36.8, and 54.3°C respectively.

Equilibrium was reached within 15 minutes at low pressures, while at pressures above 5 bar the loading in the sample kept increasing after 90 minutes and the data reported here

<table>
<thead>
<tr>
<th>Table 2.1: Constants used to fit sorption isotherms to the virial equation (Eq. 2.1).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>H, mol/(kg bar)</td>
</tr>
<tr>
<td>C$_1$, kg/mol</td>
</tr>
<tr>
<td>C$_2$, (kg/mol)$^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2.2: Constants used to fit sorption isotherms to the dual mode model (Eq. 2.2).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>m, mol/kg</td>
</tr>
<tr>
<td>K$_1$, 1/bar</td>
</tr>
<tr>
<td>K$_2$, (kg/mol)</td>
</tr>
</tbody>
</table>

|                  | Carbon dioxide       |                     |
|                  | Adsorption             | Desorption          |
| Temperature, °C | 20.3 | 36.4 | 53.4 | 20.2 | 36.4 | 53.6 |
| m, mol/kg       | -0.0158 | -0.0195 | -0.00004 | 0.0005 | 0.0054 | 0.0202 |
| K$_1$, 1/bar    | 0.029 | 0.034 | 0.026 | 0.030 | 0.012 | 0.042 |
| K$_2$, (kg/mol) | 0.206 | 0.161 | 0.110 | 0.222 | 0.156 | 0.208 |

|                  | Carbon dioxide       |                     |
| Temperature, °C | 20.3 | 36.4 | 53.4 | 20.2 | 36.4 | 53.6 |
| m, mol/kg       | 3.843 | 3.389 | 2.789 | 4.744 | 4.253 | 3.315 |
| K$_1$, 1/bar    | 0.735 | 0.453 | 0.379 | 0.548 | 0.364 | 0.312 |
| K$_2$, (kg/mol) | 0.126 | 0.098 | 0.085 | 0.092 | 0.064 | 0.065 |
do not represent equilibrium adsorption measurements. The rapid adsorption at low pressures is indicative of a microporous material while the steady gain at higher pressures could indicate polymer relaxations and swelling. There is a distinct hysteresis which closes at very low pressure in all isotherms and tends to be more pronounced at lower temperatures and with CO$_2$ in general. The hysteresis may be due, in part, to some combination of permanent deformations in the polymer allowing a greater loading at the same pressure and the inability of the polymer to elastically contract quickly enough during desorption to cause the same equilibrium loading.$^{10}$ Further discussion into the cause of the hysteresis will require more detailed study on the extent of polymer swelling and chain dynamics under sorption which is beyond the scope of the present work.

Adsorption isotherms at different temperatures can be used to calculate enthalpies of adsorption. Isotherms of at least three different temperatures need to be measured to ensure that there is sufficient data to calculate slopes with some accuracy (see Eq. 2.4). Some errors in the estimation of the enthalpy of adsorption are due to uncertainties in the measurements, while others are the result of inaccuracies in fitting the measured isotherms to empirical models. Because the calculation requires a constant loading, the maximum loading for which the enthalpy of adsorption can be calculated without extrapolation is the maximum loading of the isotherm with the lowest adsorption. Enthalpies of adsorption for methane and carbon dioxide are shown in Figure 2.3. On average, the enthalpy of adsorption of methane on PIM-1 is -18 kJ/mol, while for CO$_2$ it is -28 kJ/mol. Figure 2.3 shows clearly the large differences in enthalpies of adsorption that can be obtained from slightly different isotherm models. The unusual shape of the enthalpy of adsorption obtained with the dual mode model describes the two regimes of
adsorption: at low coverage adsorption is dominated by the Langmuirian contribution (up to about 3 mol/kg) and at higher loadings the main contribution is the dissolution in the bulk phase.

Figure 2.3: Enthalpies of adsorption and desorption of CO$_2$ (upper) and CH$_4$ (lower). Solid lines are calculated from isotherms fitted to the dual mode model and dashed lines are calculated from isotherms fitted to the virial equation.

The selectivity towards carbon dioxide was estimated using the IAST and the DM model. Figure 2.4 shows the importance of considering real gases when working at elevated pressures, as the real and ideal selectivities diverge. Deviations in selectivities estimated using a real gas model and an ideal gas approximation are between 5 and 20% at 20 bar for the systems studied. In all the results presented here, a real gas model was used. The fugacity coefficients were calculated from the Peng-Robinson equation of state using the binary interaction parameters provided in Aspen Plus$^\text{®}$. 


The temperature dependence of the selectivity was calculated using the IAST and DM model and results are shown in Figure 2.5 and 2.6. The IAST predicts a significant increase in selectivity with pressure at 20°C, but at higher temperatures the selectivity is practically independent of pressure. The DM model, on the other hand, predicts a small decrease of selectivity with pressure, with similar trends for all temperatures. As expected, both models predict a decrease in selectivity with temperature. Without
experimental data it is impossible to indicate which model is appropriate, but the measurement of mixture data is beyond the scope of this work.

Figure 2.5: IAST selectivity of carbon dioxide over methane for a constant gas phase composition ($\gamma_{\text{CO}_2} = 0.5$) and three different temperatures: 20°C (solid line), 37°C (small dashes) and 54°C (long dashes).
The IAST and DM model also predict a different composition dependence of the selectivity, as shown in Figure 2.7 and 2.8. Both models converge at low pressures, where the selectivity is independent of composition, but at high pressures the IAST predicts a higher selectivity when the gas phase is rich in carbon dioxide, whereas the DM model predicts the highest selectivity when the gas phase is rich in methane.

Figure 2.6: DM model selectivity of carbon dioxide over methane for a constant gas phase composition ($y_{CO2} = 0.5$) and at three different temperatures: 20°C (solid line), 37°C (small dashes) and 54°C (long dashes).
Additional experimental data or accurate simulations would be needed to determine which, if any, of these models is appropriate to describe adsorption of mixtures in PIMs.

Figure 2.7: IAST selectivity of carbon dioxide over methane for a constant temperature (T= 37°C) and different gas phase compositions: \( y_{\text{CO}_2} = 0.1 \) (solid line), \( y_{\text{CO}_2} = 0.5 \) (small dashes) and \( y_{\text{CO}_2} = 0.9 \) (long dashes).
Gravimetric measurements of adsorption isotherms allow the determination of the diffusion coefficients of the gas in the solid matrix after the equilibrium pressure has been reached. Although the system is not isothermal and a spike in the temperature is measurable when gas is injected, the small amount of solid used and an efficiently thermostated bath results in changes in temperature on the order of 0.2 – 0.5°C, which can be considered negligible to the use of Eq. 2.15 and 2.16 to describe the adsorption kinetics. An example of an individual adsorption point, where the pressure is increased

Figure 2.8: DM model selectivity of carbon dioxide over methane for a constant temperature (T= 37°C) and different gas phase compositions: $y_{\text{CO}_2} = 0.1$ (solid line), $y_{\text{CO}_2} = 0.5$ (small dashes) and $y_{\text{CO}_2} = 0.9$ (long dashes).
from 4 to 5 bar is shown in Figure 2.9, where the temperature and loading profiles are also indicated.

Figure 2.9: Rate of uptake of carbon dioxide on PIM-1 (dashed line) between 4 and 5 bar (long dashes). The sample temperature is shown as a solid line.

Initially, there is a brief period of rapid adsorption followed by a period of long but slow adsorption. A purely Fickian description of the adsorption process (Eq. 2.15) accounts for the rapid initial adsorption well, but fails to capture the long time behavior. By accounting for a relaxation controlled swelling process (Eq. 2.16) with just one characteristic relaxation time, the long-time behavior is well modeled. The kinetic sorption data for each differential step was modeled by the combined Fickian-relaxation model (Eq. 2.14) to determine the diffusion coefficients given in Figure 2.10, the fraction of the uptake that follows a Fickian behavior shown in Figure 2.11, and the relaxation
time for the slow adsorption process shown in Figure 2.12. Only data at the equilibrium pressure was considered to obtain the parameters shown in Figure 2.10 through 2.12.

Figure 2.10: Diffusion coefficient of carbon dioxide on PIM-1 at 20°C (open symbols) and 37°C (solid symbols).
Figure 2.11: Fraction of CO$_2$ uptake that follows a Fickian behavior at 20°C (open symbols) and 37°C (solid symbols).

Figure 2.12: Slow relaxation time constant for the adsorption of carbon dioxide on PIM-1 at 20°C (open symbols) and 37°C (solid symbols).
Figure 2.11 shows that at pressures below 2 bar, Fickian diffusion accurately
describes the kinetics of adsorption, while the slow diffusion process dominates for
pressures above 14 bar. Extrapolating the diffusion coefficients at different temperatures
to zero coverage, it is possible to obtain the activation energy of 12 kJ/mol, which is
approximately half of the absolute value of the enthalpy of adsorption. The relaxation
time constant for the slow adsorption process shown in Figure 2.12 is approximately
3000 s. The large amount of scatter in the data does not allow reliable trends to be
obtained. The relaxation time constants seem to increase with temperature and but no
clear trends are observed as a function of pressure.

Optical and electron micrographs of PIM-1 (Figure 2.13) showed that PIM-1
particles are not homogeneous and seem to consist of an agglomeration of spherical
particles, thus the model for Fickian adsorption in homogeneous spherical particles may
not be a reasonable approximation. Nevertheless, this model is useful because it allows
us to compare the properties measured in a PIM-1 powder with those reported for PIM-1
films.

Figure 2.13: (a) and (b) Optical micrographs and (c) SEM image of the PIM-1 sample
studied. Typical particle sizes shown in (b) are between 150 and 200 μm.
All diffusion coefficients for PIM-1 normalized by the characteristic length are on the order of $10^{-3} \text{ s}^{-1}$ and decrease with pressure. Assuming an average particle size of 150 µm, the diffusion coefficients obtained are between $5 \times 10^{-8} \text{ cm}^2/\text{s}$ which is similar to the reported diffusion coefficients measured in membranes of $26 \times 10^{-8} \text{ cm}^2/\text{s}$. Differences in these values may be due to the different techniques used to measure the diffusion coefficients, a non-uniform particle size and to the differences in the microstructure of processed membranes and as synthesized powder.

2.5 Conclusions

In this component of the work, data pertaining to the sorption capabilities of powdered PIM-1 as a possible adsorbent for use in gas separations have been presented. PIM-1 was shown to reversibly adsorb CO$_2$ and CH$_4$ even though a large hysteresis loop is observed due to swelling of the material. Both the adsorption isotherms and the kinetics of adsorption reveal the presence of two distinct mechanisms. At low pressures, adsorption takes place as in traditional microporous materials with the isotherm following a Langmuir model and Fickian adsorption kinetics. At high pressures the kinetics are dominated by a slow relaxation process, typical of dissolution of gases in polymeric matrices. At these conditions, the amount adsorbed is well described by a Henry’s constant.

Most industrial applications involve the adsorption of mixtures. It has been shown that two typically used models for predicting selectivity, IAST and DM model, give similar predictions at low pressures, but at high pressures the deviations are
significant. Additional experimental data of mixture adsorption would be needed to determine the validity of either model.

2.6 Bibliography

14. Budd, P. M.; McKeown, N. B. Polymer Chemistry 2010, 1, (1), 63-68.
Chapter 3
Methane Adsorption in PIM-1

The results of grand canonical Monte Carlo (GCMC) simulations of methane adsorption in a prototypical polymer of intrinsic microporosity (PIM), PIM-1, are reported. Polymer chains were represented using a united-atom model, with Lennard-Jones parameters obtained from the TraPPE potential. Additionally, partial charges were calculated from ab initio methods using Gaussian (HF/6-31G* basis set). Samples of PIM-1 were built at low density conditions, followed by a series of short NVT and NPT molecular dynamics runs in order to compress the sample to experimental densities. This protocol proved to be suitable for the realistic modeling of the amorphous structure of PIM-1. Surface areas and pore size distributions were measured and compared to available experimental data. GCMC simulations of methane adsorption were performed, and found to qualitatively and quantitatively reproduce available experimental isotherm.

3.1 Introduction

Microporous materials, defined by the IUPAC as systems with pores less than 2 nm in size, are useful in applications such as gas storage, separations, purification, and heterogeneous catalysis. Microporous materials include zeolites, activated carbons, and more recently, metal and covalent organic frameworks. Polymers of intrinsic microporosity are a new class of porous polymer based on the simple design principle
of combining monomers that are both rigid and non-planar or non-linear. These structural conditions inhibit space efficient packing and give the polymers their microporosity, but put no limitation on the chemical structure of the monomers. The wide variety of chemistries combined with the high surface areas make PIMs a promising material for a variety of applications.

Computer simulations comprise a powerful set of tools that have found many applications in the study of adsorbent materials. Classical, force field based molecular dynamics (MD) and Monte Carlo (MC) simulations are particularly well suited to study physical adsorption which is dominated by van der Waals and electrostatic interactions. This allows the exploration of real and hypothetical materials at an atomistic level of detail difficult to achieve experimentally. In this work, MD and MC simulations are utilized to increase our understanding of methane adsorption in the prototypical PIM, PIM-1 (see Figure 3.1), with the greater goal of using this knowledge to aid in the rational design of novel PIMs.
In this chapter, computer simulations are used to study the adsorption behavior of methane in PIM-1. The rest of the chapter is organized as follows. In section 3.2 the details of the preparation of the PIM-1 model and the simulations for gas adsorption are presented. Then, in section 3.3, simulated adsorption isotherms and pore size distributions are calculated and compared with available experimental results. Finally some concluding remarks and suggestions for future work are given.

3.2 Methods

The approach taken in this work to build realistic simulation samples of PIM-1 is to grow a system at a low density, chain by chain, then compress and relax the system.
via MD simulations to achieve realistic densities. Chains are randomly initiated throughout the simulation box and grown by randomly choosing one of the two chiral monomers and one of the two possible orientations until the target chain length of 10 monomers is achieved or an overlap is the result of adding either monomer type in either orientation. This results in large, low density systems of roughly 100 monomers in 10 to 14 chains, to be compressed. Systems using similar chain lengths have been studied \cite{9-11}. During the chain growth process, only hard core overlaps are avoided; all energy minimization and chain movement is done during the MD compression and relaxation. To limit the effect of chain ends on chain packing and adsorption, zero charge blocking atoms are placed at the head and tail of each chain, atoms 36 to 39 in Figure 3.1.

As specific interactions with hydrogen atoms are not expected to be significant, this work uses a united atom model in which the hydrogen atoms are grouped with the carbon to which they are bonded. Lennard-Jones (LJ) parameters were taken from the TraPPE potential \cite{12}. While the TraPPE united atom model is in general well suited to describing the system, it does not have adequate parameters to describe the oxygen atoms in the backbone. Therefore, those parameters were taken from the all atom TraPPE-EH model.

In order to assign partial charges to the monomers, a quantum mechanics calculation for a monomer model in the gas phase at the HF/6-31G* level of theory using Gaussian 03\cite{13} was carried out by collaborator Dr. Ping Lin (Materials Simulation Center, Penn State). The model monomer used in the ab initio calculations is defined as the repeating structure between two spirocenters (split at the 5 member rings rather than the 6 member aromatic rings). Capping methyl groups were placed on the joint carbon
(number 13 in Figure 3.1) between two five member rings. Afterward, a two-stage restrained electrostatic potential (RESP)\textsuperscript{14} charge fitting to the electrostatic potential was performed to obtain the partial charges. This approach and the level of theory selected have been shown to perform well for condensed phase simulations by other groups\textsuperscript{14}. All pure component LJ parameters (cross interactions calculated from Lorentz-Berthelot mixing rules) and partial charges are listed in Table 3.1 with atom numbers corresponding to Figure 3.1. Bonded parameters and further simulation details are listed in Appendix A.

Table 3.1: Simulation Parameters for PIM-1, atom numbers correspond to Figure 3.1.

<table>
<thead>
<tr>
<th>Atom Type</th>
<th>$\varepsilon/k_b$ (K)</th>
<th>$\sigma$(Å)</th>
<th>Charge (eV)</th>
<th>Number</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(aro)-O(aro)-X(aro)</td>
<td>70.0</td>
<td>2.60</td>
<td>-0.219064</td>
<td>1, 2, 3, 4</td>
<td>15</td>
</tr>
<tr>
<td>X(aro)-C(aro)-X(aro)</td>
<td>30.70</td>
<td>3.60</td>
<td>0.177839</td>
<td>7, 8, 18, 19</td>
<td>15</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.172261</td>
<td>26, 27, 29, 30</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0</td>
<td>36, 37</td>
<td></td>
</tr>
<tr>
<td>R-C(aro)</td>
<td>21.0</td>
<td>3.88</td>
<td>0.038356</td>
<td>5, 10, 16, 21</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.12304</td>
<td>28, 31</td>
<td></td>
</tr>
<tr>
<td>CH(aro)</td>
<td>50.5</td>
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<td>-0.124962</td>
<td>6, 9, 17, 20</td>
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<td>C</td>
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<td>6.4</td>
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<td>12</td>
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<td>CH$_2$</td>
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<td>17</td>
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<tr>
<td>CH$_3$</td>
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<td>22, 23, 24, 25, 38, 39</td>
<td>16</td>
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<tr>
<td>C(sp, nitrile)</td>
<td>60</td>
<td>3.55</td>
<td>0.313718</td>
<td>32, 33</td>
<td>16</td>
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<tr>
<td>N(nitrile)</td>
<td>60</td>
<td>2.95</td>
<td>-0.40999</td>
<td>35, 35</td>
<td>16</td>
</tr>
</tbody>
</table>

In search of a means to quickly and effectively compress and relax the low density initial configurations, two previously suggested MD schemes were explored\textsuperscript{18}. 

\textsuperscript{14} Lorenz-Berthelot mixing rules
\textsuperscript{15} Ref.\textsuperscript{15}
\textsuperscript{16} Ref.\textsuperscript{16}
\textsuperscript{17} Ref.\textsuperscript{17}
\textsuperscript{18} Ref.\textsuperscript{18}
The work of Hofmann et al.\textsuperscript{19}, here referred to as the 12 step scheme and outlined in Table 3.2, was originally applied successively until a consistent density was achieved. Later, Karayannis et al.\textsuperscript{20} developed several ideas to extend the 12 step scheme, such as annealing and decompression. Based off of Hoffmann’s work a new scheme, incorporating many of the ideas from Karayannis et al., has been developed. In this work, the 12 and 21 step compression and relaxation schemes are compared. The results in section 3.3 show that the 21 step slow decompression scheme with a maximum pressure of 50,000 bar and 600 K give good results, and is therefore used for the production of PIM samples in this work.

Table 3.2: Compression and relaxation schemes applied to low density initial configurations as a function of maximum pressure.

<table>
<thead>
<tr>
<th>12 Step</th>
<th>21 Step (Slow Decomp.)</th>
<th>Simulation Conditions</th>
<th>Duration (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>NVT 600 K</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>NVT 300 K</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>NPT 0.02*Pmax bar, 300 K</td>
<td>50</td>
</tr>
<tr>
<td>4,5</td>
<td>4, 5</td>
<td>NVT 600 K, NVT 300 K</td>
<td>50, 100</td>
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<td>6</td>
<td>6</td>
<td>NPT 0.6*Pmax bar, 300 K</td>
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<tr>
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<td>7, 8</td>
<td>NVT 600 K, NVT 300 K</td>
<td>50, 100</td>
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<td>9</td>
<td>9</td>
<td>NPT Pmax bar, 300 K</td>
<td>50</td>
</tr>
<tr>
<td>10,11</td>
<td>10, 11</td>
<td>NVT 600 K, NVT 300 K</td>
<td>50, 100</td>
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<tr>
<td>12</td>
<td></td>
<td>NPT 0.5*Pmax bar, 300 K</td>
<td>5</td>
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<tr>
<td>13, 14</td>
<td></td>
<td>NVT 600 K, NVT 300 K</td>
<td>5, 10</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>NPT 0.1*Pmax bar, 300 K</td>
<td>5</td>
</tr>
<tr>
<td>16, 17</td>
<td></td>
<td>NVT 600 K, NVT 300 K</td>
<td>5, 10</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>NPT 0.01*Pmax bar, 300 K</td>
<td>5</td>
</tr>
<tr>
<td>19, 20</td>
<td></td>
<td>NVT 600 K, NVT 300 K</td>
<td>5, 10</td>
</tr>
<tr>
<td>12</td>
<td>21</td>
<td>NPT 1 bar, 300 K</td>
<td>800</td>
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</tbody>
</table>

Sample densities, surface areas (SA), and pore size distributions (PSD) were measured for characterization and comparison to available experimental data. The
simulated and experimental densities are measured differently and are related by the pore volume per unit mass by Eq. 3.1:

$$\frac{1}{\rho_{\text{sim}}} = \frac{1}{\rho_{\text{exp}}} + \frac{v_{\text{pore}}}{m} \quad (3.1)$$

where $\rho_{\text{sim}}$ is the simulation density, $\rho_{\text{exp}}$ is the experimental or skeletal density, $v_{\text{pore}}$ is the pore volume, and $m$ is the sample mass (see further discussion of Eq. 3.1 below). The accessible SA of the simulation samples were measured by Monte Carlo integration\textsuperscript{21} in which a nitrogen sized probe molecule ($\sigma$ of 3.681 Å) is randomly inserted around each of the framework atoms in turn and checked for overlap with other framework atoms. The fraction of non-overlapping probe molecules is then used to calculate the accessible SA. The PSD is derived from the fractional free volume (FFV). The simulation sample is overlaid with a fine, three dimensional grid, each node of which is marked as occupied or unoccupied by the polymer. Test probes of decreasing diameter are placed at each node. The fraction of unoccupied space accessible to probes that do not overlap with the polymer matrix are summed, giving the FFV as a function of probe diameter. The negative derivative of the FFV with respect to the probe diameter gives the PSD\textsuperscript{22}.

After compression, relaxation, and characterization, simulations of gas adsorption were performed. Simulations were run in the Grand Canonical ensemble using the MCCCS Towhee code\textsuperscript{12}. Chemical potentials were calculated for methane by the ideal gas relation, Eq. 3.2:

$$\mu = k_B T \ln \frac{P A^3}{k_R T} \quad (3.2)$$
where $k_B$ is the Boltzmann's constant, $T$ is the temperature in K, $P$ is the pressure, and $\lambda$ is the de Broglie wavelength. For proper comparison to experiments, total adsorption is converted to excess adsorption via Eq. 3.3:

$$n_{exc} = n_{tot} - v_{pore} \rho_g$$  \hspace{1cm} (3.3)

where $n_{tot}$ is the total uptake, $v_{pore}$ is the pore volume, and $\rho_g$ is the gas density at the particular temperature and pressure from equation of state given on the NIST Webbook. Experimentally the polymer sample has been observed to swell slightly upon the adsorption of methane ($\Delta V/V_0 = 1.94\%$). Thus, as a first approximation in this work, we have held the polymer matrix fixed and rigid during the adsorption simulations. For each pressure step in the adsorption isotherm, simulations were equilibrated for $10^7$ steps followed by $3 \times 10^7$ steps over which averages were collected.

### 3.3 Results and Discussion

In his work from 18, Kyle E. Hart compared a single application of 12 and 21 step compression and relaxation schemes, outlined in Table 3.2, on PIM-1. Figure 3.2 summarizes the results for the slow decompression and a single application of the 12-step scheme as a function of maximum pressure for PIM-1, averaged over five boxes. The slow decompression scheme provides final simulation densities which are independent of the maximum pressure, whereas the 12-step scheme has a tendency to give lower and less consistent final densities with increasing maximum pressure. The inconsistency of the 12 step scheme, particularly at higher maximum pressures, is likely due to the dramatic release of pressure allowing for an uncontrolled decompression. Maximum temperatures
up to 1800 K were studied with both schemes, and the results (not shown) are independent of the maximum temperature selected. Thus, in this work the 21 step decompression scheme with a maximum temperature of 600 K and pressure of 50,000 bar was used. All MD simulations were performed using LAMMPS\textsuperscript{24} with the Nosé-Hoover thermostat and barostat\textsuperscript{25}.

![Figure 3.2](image.png)

**Figure 3.2**: Comparison of the resulting simulation density from a single application of the 12 step (■) and 21 step (●) compression and relaxation schemes on 5 samples of PIM-1 as a function of maximum pressure. The dramatic release of high pressures in the 12 step scheme allows the polymer to spring apart creating lower density systems with a higher degree of variability.

As the number of computations increases rapidly with the number of particles in the simulation, it is desirable to use as small of a sample as possible. This tendency towards smaller samples needs to be balanced such that the size of the sample does not affect the simulation results\textsuperscript{26,27}. Because adsorptive properties are heavily dependent
on SA and PSD, the optimal sample size was determined by comparing the SA and PSD for ten samples of 32, 45, and 55 Å which were compressed, as described above, from 70, 100, and 120 Å, respectively. No significant variation in SA between individual samples or sample sizes was observed. As the PSD is the negative derivative of the FFV, differences between sample sizes are more easily seen in the FFV. In Figure 3.3, the FFV as a function of probe size for ten samples of each of the three box sizes, are shown. There is a wide variability in FFV for the 32 Å samples with an average value much higher than that of the 45 and 55 Å samples. The FFV for the 45 and 55 Å samples have similar variability, thus the 45 Å sample is chosen as the optimal box size balancing pore size consistency with computational efficiency.

3.3: The FFV as a function of probe size for 10 samples of 32 (●), 45 (■), and 55 (+) Å boxes. The 45 Å boxes offers nearly the same consistency as the 55 Å boxes, but at significantly reduced computational costs, making it the ideal box size for this work.
Simulation samples were characterized by their density, SA, and PSD. Each of these quantities can be calculated from simulations and measured experimentally. However, a comparison between the simulation and experimental results requires care. For example, the key difference between simulation and experimental calculations of the density is that experiments measure the skeletal volume while simulations use the total volume of the simulation box. That is, experimentally the material is submerged in an inert fluid (such as helium) to measure the buoyancy which used to calculate the density. The experimentally calculated density uses the dry sample mass and the volume inaccessible to the probe fluid. That inaccessible volume is the space taken up by the atoms of the material or the skeletal volume. Thus, the simulated and experimental densities differ by the pore volume according to Eq. 3.1. Experimentally, we measured the density of a powdered PIM-1 sample to be 0.94 g cm$^{-3}$ via helium pycnometry 28 while other works have measured a density of 1.06-1.09 g cm$^{-3}$ in films via measurement of the sample weight in air and in the fluorocarbon fluid Fluorinert FC-77 29, and 1.4 g cm$^{-3}$ for films via helium pycnometry 9. From simulations of helium adsorption, the pore volumes for the 45 Å sample can be calculated by Eq. 3.4 30:

$$v_{pore} = \frac{n_{ads}}{\rho_{He}}$$  

(3.4)

where $\rho_{He}$ is the density of helium at 1 bar, 20 C, $v_{pore}$ is the pore volume per unit mass, and $n_{ads}$ is the amount of He in the sample. The pore volume was calculated as 0.194 +/- 0.0164 cm$^3$ g$^{-1}$ such that the simulated density of 0.975 +/- 0.0154 cm$^3$ corresponds to a skeletal density of approximately 1.202 +/- 0.00972 g cm$^{-3}$ (averaged over five samples).
The PSD is a derived quantity in both simulations and experiments, thus comparing PSDs from different methods is fraught with difficulties in reconciling the different techniques and their underlying assumptions. In Figure 3.4, we show a plot of experimental PSDs derived from the Horvath-Kawazoe (HK) method\(^{31}\), Positron Annihilation Lifetime Spectroscopy (PALS)\(^{32}\) and the geometric PSD from simulations for the 45 Å samples from the FFV. All three techniques compared have their limitations, for example, the HK data in Figure 3.4 shows a strikingly sharp low pore size cutoff. The low pore size resolution limit is effected by the low pressure limit of the experimental apparatus; the contributions from pores below this limit are grouped in with the first measurable pores creating an inflated peak near the limit of the instrument. PALS requires the researcher to deconvolute the recorded spectra and choose the number of modes in the distribution. The PALS data\(^{32}\) were interpreted as a bimodal PSD. Taking for granted the theory and models used to make a simulation sample, the pore size distributions are calculated geometrically, sidestepping the complex models and assumptions required by experimental techniques. Thus, the simulated PSD may be used to guide the experimental interpretation of data.
A Gaussian curve provides a good fit to the FFVs (as in Figure 3.3) in that it accurately reproduces the curve shape, exponentially decays for large pore sizes, and has a simple derivative. Fitting the FFV for the 45 Å samples according to:

\[ FFV = a e^{-\frac{x^2}{2c^2}} \]  \hspace{1cm} (3.5)

gives the parameters \( a \) and \( c \) of 0.567 and 3.47 respectively. The PSD is taken as the negative of the derivative of the FFV:

\[ PSD = -\frac{d}{dx} FFV = \frac{ax}{c^2} e^{-\frac{x^2}{2c^2}} \]  \hspace{1cm} (3.6)

with \( A \) equal to 0.0469 and a maximum at a pore diameter of 3.48 Å.
Generally, the simulated PSD in Figure 3.4 suggests that the PALS data may be better interpreted as a broad unimodal distribution and that the HK data may underestimate the degree of ultramicropores. It is worth noting that the simulation samples, due to the finite size of the sample, do not accurately model the larger micropores or mesopores that may be present experimentally. Thus, experimentalists wishing to fit their data with Eq. 3.6 may require parameters that allow for a broader peak or other features at larger size scales.

Surface areas for ten 45 Å boxes were calculated with an average value of 448.986 +/- 85.183 m²/g. Experimentally, PIM-1 is reported to have a BET surface area of 750 to 860 m²/g. The deviation between simulated and experimental values may be attributed in part to the ultramicroporous nature of PIMs causing an overestimation by the BET method.

After the sample was characterized, GCMC simulations of methane adsorption were performed. The simulated adsorption isotherm is plotted against the experimental isotherm for powdered PIM-1, in Figure 3.5. The simulation qualitatively and quantitatively reproduces the experimental isotherm. The simulations were run to higher pressures to investigate limiting behavior; minimal uptake was observed between 20 and 55 bar. The slight overestimation of adsorption capacity compared to experimentally measured values may be due in part to differences in sample histories and pore accessibility. PIM-1 can be made from several different polymerization techniques and subsequently be precipitated into a powder or cast into a film. Further adsorption experiments testing different sample histories would be insightful in further determining the quality of the model. Due to the nature of GCMC simulations, experimentally
kinetically inaccessible pores may be filled, adding to the overestimation. Future work will look to investigate the proportion of inaccessible pores in the simulation samples.

Figure 3.5: Simulated (■) methane adsorption in PIM-1 at 20 C compared to the corresponding experimental data (+)\textsuperscript{28} for a powdered sample of PIM-1.

3.4 Conclusions

In this chapter, molecular simulation results for methane adsorption on a united-atom model of PIM-1 have been reported. A detailed investigation of the structure of other gases inside these pores, as well as similar PIMs with other functionalities, such as fluorine and aromatic nitrogen are currently underway in our group, and could be relevant
for ongoing research in heterogeneous catalysis, purification, separations, and gas storage.

3.5 Bibliography

Chapter 4

Novel PIM-1 Like Polymers, Characterization and Methane Adsorption

Polymers of Intrinsic Microporosity, or PIMs, are characterized by rigid and nonlinear or nonplanar backbones that inhibit space efficient packing, thus creating microporosity. PIM-1 has been well studied by both simulations and experiments and is compared in this work to three new structural variations. The structure generation technique detailed in the last chapter is applied to several novel structures. Physical characterization and methane adsorption for each structure are presented and compared.

4.1 Introduction

Gas adsorption is an important process with many applications, including gas storage and separations. As necessity to use energy efficient and environmentally friendly processes increases, so too do the requisites for the design and development of tailor made adsorbent materials. While all solids are capable of adsorption, the vast majority lack sufficient capacity and selectivity for practical use. An ideal material for adsorption and separations will have a combination of micropores (size less than 2 nm) to give high capacity and selectivity, and meso- or macro- pores (between 2 and 50 nm, and larger than 50 nm, respectively) to give fast sorption kinetics (pore sizes named according to IUPAC convention\(^1\).\(^2\)).
To date, a wide range of microporous materials have been investigated. Two broad classes of materials are crystalline and amorphous materials typified by activated carbons and zeolites\textsuperscript{2, 3}. Due to the low costs, high surface areas (SA), and large sorption capacities, activated carbons are widely used in industry. Zeolites can occur naturally or be synthesized and are commonly used in kinetic separations and catalysis. Chemically, the different zeolites are very similar, typically aluminosilicates or aluminophosphates, but vary widely in pore topology. Of more recent interest, metal organic frameworks\textsuperscript{4}(MOFs) (also known as porous organic frameworks, porous coordination polymers,\textit{etc.}), consist (usually) of metal ligands separated by rigid organic linkers. By varying the ligand and/or linkers, a large number of structures can be made. MOFs have been demonstrated to have extremely high SAs of up to 6000 m\textsuperscript{2} g\textsuperscript{-1}. Snurr and coworkers have used molecular simulations extensively to study and screen novel MOF architectures and enhance understanding of the adsorption process\textsuperscript{5, 6}. For a complete reviews of microporous materials the reader is referred, \textit{e.g.}, to references\textsuperscript{2, 3} and references therein.

The light weight organic constituents, functionalizability, and potential for industrial scaling are making polymers attractive as potential microporous materials. However, the generally flexible nature of polymers allows for space efficient packing with almost no micropores and hence poor material properties for storage and separations. To date, several porous polymers have been created\textsuperscript{7}. One example, hypercrosslinked polymers, are made by extensive crosslinking of a swollen polymer using rigid crosslinkers such that the microporosity is generally maintained after solvent removal. Various groups have used a combination of simulations and experiments to investigate these materials\textsuperscript{8-10}.
Polymers of intrinsic microporosity (PIMs) represent a novel class of porous materials that derive their porosity not from processing conditions, but from their unique molecular structure, which inhibits space efficient packing\textsuperscript{11}. By creating monomers that are both rigid and non-linear or non-planar, the resulting polymeric material develops a microporous structure. PIMs with SAs in excess of 1000 m\textsuperscript{2} g\textsuperscript{-1} of BET SA have been recently synthesized\textsuperscript{12}. PIMs have shown hydrogen uptakes as high as 1.83 wt\% at 0.1 MPa and 77 K\textsuperscript{12} and are pushing the Robeson upper bound of permeability and selectivity\textsuperscript{13}.

Molecular simulations represent a powerful and widely used tool for the investigation and study of adsorbent materials. Classical molecular dynamics (MD) and Monte Carlo (MC) simulations are particularly well suited to the study of physical adsorption because the phenomenon depends primarily on van der Waals and electrostatic interactions between the sorbent and the sorbate. While experiments provide physical data, they are often hindered by limitations in the equipment, sample quality, and interpretive models. Molecular simulations can help by looking at ideal systems, experimentally inaccessible conditions, and by providing a high level of detail (often atomistic). Simulations can not only be used to study adsorption, but also to calculate key materials properties such as pore size distributions (PSD), SAs, structure factors, enthalpies of adsorption, and selectivities of gas mixtures. Furthermore, simulations can be applied to both realized and conceptualized materials and used in materials screening and design.

The aim of this research is to aid in the rational design of novel PIMs for application in gas storage and separations. The work presented here focuses on the
preparation, characterization, and adsorption capabilities of a realistic simulation sample of PIM-1 and three bi-functional polymers, in this work called PIM-1c, PIM-1n, and PIM-1f. Both PIM-1c\textsuperscript{14} and PIM-1n\textsuperscript{15} have been recently synthesized, while PIM-1f represents an as yet unsynthesized theoretical limiting case. While it may not be possible to synthesize such a polymer, its exaggerated differences compared to the other functional variations of PIM-1 will help highlight the differences and deepen our understanding of more physically realistic polymers. PIM-1 is the prototypical example of PIMs and has been extensively studied from an experimental point of view. PIM-1c and PIM-1n were chosen because they represent small and controlled changes to the PIM-1 structure and have been synthesized; however to date, minimal experimental characterization data exist. The similarities between the four samples allow for the effects of the functional changes on the material’s characteristics and properties to be isolated, while the potential for synthesis will allow for experimental verification. Methane was chosen as the adsorbate for both its simplicity and to isolate the effects of the conformational alterations from electronic changes of the materials by adsorbing neutral species.

4.2 Methods

The generation of a realistic simulation sample for amorphous materials is still a challenge. For crystalline materials, various diffraction techniques can be used to experimentally derive the structure of the unit cell. These structures are an invaluable starting point for simulations and are unavailable for amorphous materials such as PIMs.
The so-called reconstruction techniques attempt to create simulation samples that reproduce a given set of experimental data. For polymeric materials, the method of Theodorou and Sutter is widely used, even for PIM-like structures. Other complex amorphous materials, such as activated carbons and porous glasses, often use a reverse Monte Carlo (RMC) technique, in which additional MC criteria are used to guide the sample structure generation toward reproducing some experimental data, such as structure factors or correlation functions.

In the case of PIMs the creation of the packing model, especially one that accurately represents the material, is nontrivial. The chemical structure of the repeat units of PIM-1, PIM-1c, PIM-1n, and PIM-1f are shown in Figure 4.1; the spirocenter at the junction of the two five membered rings can create a nearly right angle bend into or out of the page resulting in two distinct chiralities. In this work, chains are randomly initiated throughout the simulation box and grown in a stepwise manner, by randomly choosing one of the two chiralities and one of the two possible orientations, until the target chain length is achieved or an overlap results from any further growth. Ultimately, the growth stage is completed when a target density is achieved. The system is grown at a low density, approximately 0.07 g cm$^{-3}$, similar to other simulations of glassy polymers that contain aromatic moieties. This procedure allows chains to grow without hard core overlaps.
While it is common practice in molecular simulations of polymers to use a single long chain to reduce the effects of chain ends, the rigid and awkward structure of PIMs makes this impractical. Thus, chain growth was generally terminated after 10 monomers were added or an overlap resulted from any further additions, as in previous work\textsuperscript{20}, resulting in samples of approximately 10 to 15 chains in the simulation box. Charge-neutral steric blocking groups were added to the chain ends to eliminate any high-energy sites and reduce the effect of the higher chain end density in the simulations.

The low-density initial structure, described above, is transformed, as in the previous chapter, by a series of short NVT and NPT MD runs into a sample of realistic density. MD simulations are performed using LAMMPS\textsuperscript{27} with the Nosé-Hoover thermostat and barostat. As there are no hydrogen atoms capable of hydrogen bonding

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Chemical structure of (a) PIM-1, (b) PIM-1c, (c) PIM-1n, and (d) PIM-1f. Numbers correspond to simulation parameters listed in Table 4.1}
\end{figure}
present in the PIMs studied in this work, the polymers are described here using a united atom (UA) representation. Non-bonded interaction parameters are taken from the TraPPE potential\textsuperscript{28} and charges from \textit{ab initio} calculations performed by collaborator Dr. Ping Lin. Bonded interaction parameters, as suggested by the TraPPE potential, are obtained from the GAFF\textsuperscript{29} force field. Due to the highly delocalized electron structure of the polymer, charges from \textit{ab initio} calculations were used. Charges were determined similarly to previous work\textsuperscript{20} using calculations for monomer models in the gas phase at the HF/6-31G* level of theory followed by a restrained electrostatic potential (RESP)\textsuperscript{30} charge fitting with multiple configurations. All pure component LJ parameters (cross interactions calculated according to Lorentz-Berthelot mixing) and charges from \textit{ab initio} calculations used in this work are listed in Table 4.1.
Table 4.1: Nonbonded interaction parameters for the simulations of PIM-1c, PIM-1n, and PIM-1f; numbers correspond to Figure 4.1.

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<th>σ (Å)</th>
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<th>Charge (eV)</th>
<th>PIM-1n</th>
<th>Charge (eV)</th>
<th>PIM-1f</th>
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Experimentally, the skeletal volume is measured, while in molecular simulations the total box volume is considered. Thus the simulated density differs from the experimentally measured skeletal density by the pore volume per unit mass according to Eq. 3.1. From simulated helium adsorption, the pore volume can be calculated according to Eq. 3.4.

It is common in simulations to utilize periodic boundary conditions both to ensure the simulation of bulk material properties and maximize the computational efficiency by limiting the number of particles in the system. Amorphous materials, lacking the natural periodicity of a unit cell found in crystalline materials, require the simulation sample to be sufficiently large to include features of the largest length scale of interest observed in the material experimentally. The key feature in a porous material is the size of the pores, which is related to the fractional free volume (FFV). A comparison of FFVs for different size samples of PIM-1 was previously used to determine the optimal box size. The results from chapter 3 found the 32 Å sample to have a wide variability in FFV while the 45 and 55 Å samples were similar suggesting that the 45 Å sample size provides the smallest yet sufficient size. Simulated density and scattering appeared consistent at all box sizes. Due to their structural similarities to PIM-1, a sample size of 45 Å is assumed to be sufficient for PIM-1c, PIM-1n, and PIM-1f.

Simulation samples are subjected to grand canonical Monte Carlo (GCMC) simulations to calculate excess adsorption isotherms. GCMC simulations were performed with the MCCCS Towhee code. The input chemical potentials were calculated according to the ideal gas approximation (which can be considered valid over the temperature and pressure ranges studied in this work) Eq. 4.1:
\[ \mu = k_B T \ln \frac{P A^3}{k_B T} \]  

(4.1)

where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature in Kelvin and \( A \) is the de Broglie wavelength. As experiments measure the excess adsorption, simulation data must be converted from total adsorption according to Eq. 4.2:

\[ n_{\text{exc}} = n_{\text{tot}} - v_{\text{pore}} \rho_g \]  

(4.2)

\( n_{\text{tot}} \) is the total uptake, \( v_{\text{pore}} \) is the pore volume from helium adsorption simulations, and \( \rho_g \) is the gas density at the particular temperature and pressure from the NIST Webbook \(^{39}\).

**4.3 Results and Discussion**

**4.3.1 Characterization**

As seen in chapter 3, the 21 step slow decompression scheme creates samples with experimentally realistic densities for PIM-1. As no densities have been reported for PIM-1c, PIM-1n, or PIM-1f, they are reported in Table 4.2 as predictive values. The calculated skeletal densities are useful for comparison to experimental data; however, due to the derived nature of the skeletal density, the simulation density is more useful for comparison and interpretation of the simulation results. As will become important in later discussion regarding adsorption capacity, the densities increase from smallest to largest from PIM-1n, PIM-1, PIM-1c, and PIM-1f.
Numerous definitions of SA can be used, but it has been suggested that the solvent accessible SA is most appropriate for comparison to BET SAs. Experimental BET SAs for PIM-1 have been reported from 750 to 860 m$^2$/g, and as 501 m$^2$/g for PIM-1c. The simulated solvent accessible SA of PIM-1, PIM-1c, PIM-1n, and PIM-1f averaged over 5 samples are reported in Table 4.2 based on a nitrogen size probe of 3.68 Å. The geometric SA calculated for PIM-1 here is similar to the GCMC nitrogen adsorption based calculation of 435 m$^2$/g by Heuchel et al. on their PIM-1 systems. The simulations correctly predict the SA of PIM-1 and PIM-1c relative to one another, but give generally lower values. Possible sources of this deviation may include experimental model assumptions (e.g., slit pores or nitrogen interaction parameters) or differences in sample histories.

Calculation of the structure factor from simulation samples is a well established practice. Simulated scattering was performed using ISAACS with structural data averaged over ten snapshots taken during a 500 ps NVT run at the end of the compression and relaxation scheme described above. The scattering data are calculated from partial radial distribution functions by Eq. 1.9:

$$I(q) = \langle \rho \rangle \int dr \frac{4\pi r^2}{q} \sin qr \sum_{a,b} f_a x_a f_b x_b [g_{ab}(r) - 1]$$  \hspace{1cm} (4.3)
where $I(q)$ is the scattering intensity as a function of wave vector $q$, $\rho$ is the average number density of the system, $g_{ab}$ is the partial radial distribution function of atomic species $a$ and $b$, $f$ is the scattering length and $x$ is the mole fraction of each species in the system. As this work uses a UA model, a first approximation of the scattering pattern was calculated ignoring contributions from hydrogen. This approximation is justified by both the small scattering length of hydrogen and the small mole fraction of hydrogen in all PIMs studied here.

Simulated scattering patterns for PIM-1 are compared to experimental WAXS data\textsuperscript{46} in Figure 4.2. Despite the variation at low $q$, the simulated scattering patterns all reproduce the three characteristic peaks (marked in Figure 4.2b). The scattering vector $q$ is inversely proportional to distance, thus the low $q$ values represent longer lengths and the low $q$ limit is defined by the size of the simulation sample. In the low $q$ region, greater variation between samples is observed as an inherent consequence of box size limitations and periodic boundary conditions. At intermediate $q$ values, representative of length scales comparable to pore size and chain spacing, all samples converge and give results consistent with experimental data. At the highest $q$ values, deviations are again observed between the simulations and experiments, here likely due to the assumption of $q$ independent scattering lengths in the simulations. Analysis of the partial structure factors from simulations suggests that the characteristic peaks and the slope on which they are superimposed are indicative of interchain spacing and intersegmental distances\textsuperscript{46}. 
Figure 4.2: (a) A single representative simulated scattering pattern of PIM-1 (-) which reproduces the slope and characteristic peaks observed experimentally in the methanol treated film and untreated powder of PIM-1 (● and ■, only every 75th data point is indicated with a symbol)46. (b) Simulated scattering patterns for multiple simulation samples of PIM-1 are compared to one another (solid lines) and to experimental data of a methanol treated film (●) and non-methanol treated powder (■) from46.
Simulated scattering was performed in the same manner on PIM-1c, PIM-1n, and PIM-1f. In all cases, wider variability is observed at low q, while all samples of a given type collapse at higher q values. Single representative scattering patterns for samples of PIM-1c, PIM-1n, and PIM-1f are compared to PIM-1 in Figure 4.3. All the PIMs show a strong peak near 1 and 1.3 Å\(^{-1}\). PIM-1f lacks the final peak at 1.6 Å\(^{-1}\) seen in the other PIMs. The origin of this behavior is not well understood, but is likely related to the lack of nitrile functionality. PIM-1, PIM-1c, and PIM-1n, despite varying spirocenter functionality, maintain similar scattering patterns and all have at least one nitrile group on the backbone while PIM-1f does not.

Figure 4.3: Representative simulated structure factor for PIM-1c (■), PIM-1n (♦), and PIM-1f (▲) compared with calculations for PIM-1 (●). Of significant interest is the fact that PIM-1f appears to be missing the 1.6 Å\(^{-1}\) peak observed in the other three PIMs.
Characterization is continued by considering the PSD. The PSD is critical in understanding the adsorption process at the microscopic level, but is difficult to measure experimentally. Two of the most common experimental techniques are the Horvath-Kawazoe (HK) method \(^ {47}\) and Positron Annihilation Lifetime Spectroscopy (PALS) \(^ {48}\). In both methods, complex models and assumptions are used to transform the experimental data into a PSD. Given a realistic simulation sample, molecular simulations can directly measure the FFV and PSD geometrically with no complex models or assumptions, and may therefore be useful in interpreting experimental data. The FFV is used to derive the PSD by taking the derivative with respect to the pore width \(^ {49}\). PSDs for PIM-1, PIM-1c, PIM-1n, and PIM-1f were calculated as in Chapter 3 according to

\[
FFV = \alpha e^{-\frac{x^2}{2c^2}}
\]

\[
PSD = -\frac{d}{dx} FFV = \frac{ax}{c^2} e^{\frac{x^2}{2c^2}} = Ax e^{\frac{-x^2}{2c^2}}
\]

and are compared in Figure 4.4. The similar chemical structures of PIM-1, PIM-1c, PIM-1n, and PIM-1f produce similar PSDs, a broad peak around 3.5 Å with a tail leading to larger pores. The parameters to Eq. 4.4 are compared in Table 4.3.
By comparing the radial distribution functions (RDF) of the spirocenter carbons in each structure (the atom at the junction of the five member ring in Figure 4.1), some insight into the PSD variations can be elucidated. The radial distribution function, $g_{a,b}(r)$, gives the density of $b$ in the shell of inner radius $r$ and outer radius $r+dr$ around any atom $a$ normalized to the bulk density of $b^{50}$. In Figure 4.5, the spirocenter-spirocenter RDFs

Table 4.3: FFV and PSD fit parameters and peak positions

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$c$</th>
<th>$A$</th>
<th>PSD Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1</td>
<td>0.567</td>
<td>3.47</td>
<td>0.0469</td>
<td>3.47</td>
</tr>
<tr>
<td>PIM-1c</td>
<td>0.494</td>
<td>3.04</td>
<td>0.0533</td>
<td>3.04</td>
</tr>
<tr>
<td>PIM-1n</td>
<td>0.575</td>
<td>3.61</td>
<td>0.0441</td>
<td>3.61</td>
</tr>
<tr>
<td>PIM-1f</td>
<td>0.494</td>
<td>3.73</td>
<td>0.0356</td>
<td>3.72</td>
</tr>
</tbody>
</table>

Figure 4.4: Simulated PSD for PIM-1 (○), PIM-1c (■), PIM-1n (♦), and PIM-1f (▲) averaged over 10 samples. PIM-1f shows PSD peak position between PIM-1 and PIM-1c with slightly higher probability of large pores.
for each structure are compared. The 15 Å peak seen for all polymers is from adjacent spirocenters along the same chain while the peaks at shorter distances are attributed to interchain spirocenter spacing and depend on the spirocenter functionality. The interchain peaks go from PIM-1f, to PIM-1 and PIM-1n, to PIM-1c in order of decreasing distance according to the decreasing volume of the functional groups. PIM-1f was designed, in part, to have bulkier spirocenter functionalization to increase interchain spacing and hence pore size. Looking at the RDFs, this seems to have worked. However, looking at the PSDs in Figure 4.4, one cannot draw the same conclusion. PIM-1f shows a PSD peak between that of PIM-1 and PIM-1c though there is a nominally higher probability of larger pores. This failure to increase the average pore size may be due in part to pore filling effects caused by the large volume of the CF$_3$ backbone functionality in PIM-1f. The lower magnitude of the PIM-1f PSD peak is due to the lower geometric pore volume (the volume enclosed by the Connolly surface) as opposed to that which is accessible to a helium probe.
Adsorption

Simulated excess adsorption isotherms for PIM-1, PIM-1c, PIM-1n and PIM-1f \(^\text{20}\) are plotted along with experimental data for methane adsorption in PIM-1 at 20 C, in Figure 4.6\(^\text{52}\). PIM-1c and PIM-1n represent stepwise functional changes to PIM-1, and show methane adsorption isotherms that are nearly identical. In all cases, the shape of

---

**Figure 4.5:** Plot of the spirocenter-spirocenter radial distribution function for PIM-1 (●), PIM-1c (■), PIM-1n (♦), and PIM-1f (▲). All polymers show a prominent peak at 15 Å from adjacent spirocenters on the same chain. At shorter distances, the peak can be attributed to interchain spirocenter spacing and is located according to the volume of the spirocenter functional group. PIM-1c has the lowest volume spirocenter functionalization with a carbonyl oxygen, while PIM-1 and PIM-1n both have methyl groups and show overlapping peaks, and PIM-1f has the highest volume trifluoromethyl groups.
the isotherm is qualitatively reproduced, and in the case of PIM-1, good quantitative agreement with experimental data is achieved.

Figure 4.6: CH₄ adsorption as a function of pressure in PIM-1 (●), PIM-1c (■), PIM-1n (♦), and PIM-1f (▲) compared to experimental data for PIM-1 (+) (Larsen TBS), all at 20 C.

Examining the differences between the adsorption isotherms for each polymer in more detail, one notices that adsorption capacity decreases from PIM-1n, to PIM-1 and PIM-1c, to PIM-1f. While the loading of PIM-1c is quantitatively similar to PIM-1, the shape of the isotherm shows greater adsorption at low pressures and a lower maximum uptake. The stronger uptake at low pressures follows from the smaller average pore size seen in Figure 4.4 while the lower maximal uptake follows from the smaller pore volume.
PIM-1n shows a larger adsorption capacity while PIM-1f shows lower adsorption capacity than the other polymers. While both PIM-1n and PIM-1f have nearly identical pore volumes, of the four polymers considered here, PIM-1f has the highest density while PIM-1n has the lowest. Thus, as the adsorption capacity is considered per unit mass, PIM-1f pays a penalty for having such a large density while PIM-1n benefits from such a small density. When the volumetric uptake is considered, as opposed to the gravimetric uptake plotted in Figure 4.6, the difference between PIM-1f and the other polymers is reduced, though not eliminated, as shown in Figure 4.7.

Figure 4.7: Adsorption data from Figure 4.6 replotted volumetrically for CH₄ in PIM-1 (●), PIM-1c (■), PIM-1n (♦), and PIM-1f (▲).

The lower volume carbonyl oxygen atoms of PIM-1c allow for closer chain packing creating a higher density system with lower pore volume and surface area. The
effect of substituting an aromatic nitrogen along the backbone in PIM-1n are less clear, but create a system with slightly larger pores and surface areas than PIM-1. Based on the RDFs, PIM-1f’s larger spirocenter functionality helps to increase chain spacing, though a corresponding increase in pore size and adsorption is not seen, possibly due to pore filling. From this work, we can conclude that 1) spirocenter functionality influences chain spacing, 2) the effect of pore filling by the functional groups needs further investigation, and 3) the system density influences storage density meaning creative use of lightweight constituent elements in monomer design is important in meeting particular gravimetric or volumetric storage targets.

4.4 Conclusions

In this chapter, the chain growth and 21 step slow decompression scheme successfully applied to PIM-1 was extended to three novel polymers. PIM-1c has been synthesized but minimally characterized, PIM-1n has been proposed, and PIM-1f represents an experimentally challenging structure that is studied via simulations to highlight the effect of various functional changes to the PIM-1 structure. For the novel polymers studied here, calculated SAs, PSDs, densities, and scattering patterns are consistent with PIM-1 and our expectations. Methane adsorption isotherms for the novel polymers show similar behavior to that of PIM-1, but suggest that future work should focus on the development of polymers with increased backbone rigidity and increased chain spacing. However, these targeted changes need to be weighed against the effect of pore filling and increased density in order to maintain high performance.
4.5 Bibliography

46. McDermott, A. G.; Larsen, G. S.; Budd, P. M.; Colina, C. M.; Runt, J. *Macromolecules* **2010**.
Chapter 5

CO$_2$, N$_2$, and O$_2$ adsorption in PIM-1 and its Functional Variations

The aim of the work presented here is build off the previous chapters by exploring the adsorption of polar gases in polymers of intrinsic microporosity (PIMs), specifically PIM-1 and several functional variations including a novel fluorinated polymer, PIM-1f. Despite the sizeable and growing body of research on PIMs, a greater understanding of the relation between the monomer, bulk solid, and polymer-gas interaction is of significant interest. Previous work has demonstrated the wide range of possible spirocenter and backbone chemistries as well as more systematically explored variations on PIM-1. While researchers have shown that PIMs are tunable to a certain extent, the design principles to tailor PIMs to specific applications remain to be determined. We present here carbon dioxide (CO$_2$), oxygen (O$_2$), and nitrogen (N$_2$) adsorption from grand canonical Monte Carlo (GCMC) simulations in PIM-1 and previously introduced functional variations of PIM-1c, PIM-1n, and PIM-1f.

5.1 Introduction

Current environmental and economic pressures are demanding increasingly energy efficient and environmentally friendly practices at all levels of society. Microporous materials, defined by IUPAC as materials with pore sizes less than 2nm$^1$, will play an important role in fulfilling those demands with respect to gas separation and
storage as well as catalysis. Microporous materials offer a safe and efficient means to store green fuels, such as methane or hydrogen, via physical adsorption as well as the ability to separate and purify those and other industrially important gasses kinetically as a membrane or via adsorptive selectivity.

While microporous materials, such as zeolites and activated carbons, have been known for thousands of years, the past two decades have seen major advances in the synthesis of microporous materials. Metal organic frameworks (MOFs are also known as porous coordination polymers, etc.) have been the subject of recent and intense research efforts\textsuperscript{2-5}. MOFs contain several key features that make them such interesting microporous materials, namely the wide range of constituent groups that can be mixed and matched to create an extremely large number of materials and the control of pore size and chemistry to suite each particular application. Similar to MOFs, polymers can be functionalized and their chemistry tuned at the monomeric level and they offer the additional advantage of flexibility and large scale processability, making them ideal candidates for membranes and gas storage materials.

In contrast to hypercrosslinked polymers\textsuperscript{6-8}, which derive their porosity from rigid crosslinks formed during a solvent swollen state, polymers of intrinsic microporosity (PIMs) rely on space inefficient packing induced by rigid backbone segments connected by nonlinear or nonplanar sites of contortion\textsuperscript{9-11}. While there is no limit to the specific chemistry involved, PIMs typically rely on fused aromatic rings to form a rigid ladder like polymer backbone. The prototypical and most widely studied example, PIM-1, relies on a 1,1-spirobisindane, here referred to simply as the spirocenter, which acts as a site of
contortion by providing a rigid right angle bend in the chain backbone. The chemical structures of the PIMs investigated in this work are given in Figure 5.1.

![Chemical structures](image)

Figure 5.1: Chemical structures of (a) PIM-1, (b) PIM-1c, (c) PIM-1n, and (d) PIM-1f. All polymers are based on the 1,1-spirobisindane site of contortion but vary in spirocenter and backbone functionality; numbers correspond to Table 3.1 and Table 4.1.

Despite the sizeable and growing body of research on PIMs, a greater understanding of the relation between the monomer, bulk solid, and polymer-gas interaction is of significant interest. Previous work has demonstrated the wide range of possible spirocenter and backbone chemistries\(^9\) as well as explored more systematic variations on PIM-1\(^{12-14}\). Weber et al.\(^{15}\) have shown that increasing the degree of polymer-polymer interaction decreases porosity and pore size and suggested, in addition to creating a tailored material, creating a material that can reversibly change its properties post synthetically. While researchers have shown that PIMs are tunable in terms of
selectivity, one generally sees movement parallel to the Robeson upper bound, not perpendicular.

Simulations of PIM-1 systems have been undertaken in attempt to compliment and extend experimental works\textsuperscript{16-19}. Simulations provide a detailed atomistic view of the polymer-polymer and polymer-gas interactions and can often augment the experimental findings\textsuperscript{20,21}. As simulations are based on a detailed knowledge of atomic positions, geometric calculations of key materials properties such as surface areas and pore sizes can be performed and avoid many complex models and assumptions required for the interpretation of experimental data. Additionally, simulations may be used to explore the performance potential of novel materials.

The aim of the work presented here is to build off previous research by exploring the adsorption of polar gases in PIM-1 and several functional variations described in chapter 4, namely PIM-1c, PIM-1n, and PIM-1f shown in Figure 5.1. In this chapter CO\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2} adsorption via GCMC simulations in PIM-1 and its functional variations is presented.

5.2 Methods

5.2.1 Simulation Details

The polymer relaxation and compression MD simulations, described in chapter 3, are performed using LAMMPS\textsuperscript{22} with the Nosé-Hoover thermostat and barostat. As there are no hydrogen atoms capable of hydrogen bonding present in the PIMs studied in this
work, the polymers are described here using a united atom (UA) representation. Non-bonded interaction parameters are taken from the TraPPE potential\textsuperscript{23} and bonded parameters, are taken from the GAFF\textsuperscript{24}. Parameters for PIM-1, PIM-1c, PIM-1n, and PIM-1f are as given in previous chapters. As designated in the TraPPE potential, CO\textsubscript{2}, N\textsubscript{2}, and O\textsubscript{2} are modeled as three center Lennard-Jones (LJ) molecules; in the case of N\textsubscript{2} and O\textsubscript{2}, a point charge is located at the center of mass which has LJ parameters and mass of zero; parameters and relevant physical properties are given in Table 5.1. Due to the highly delocalized electron structure of the fused aromatic ring forming the polymer backbone, charges are taken from \textit{ab initio} calculations for monomer models in the gas phase at the HF/6-31G* level of theory followed by a restrained electrostatic potential (RESP)\textsuperscript{25} charge fitting with multiple configurations.

### Table 5.1: LJ parameters for CO\textsubscript{2}\textsuperscript{26}, N\textsubscript{2}\textsuperscript{26}, and O\textsubscript{2}\textsuperscript{27} from the TraPPE potential and relevant physical properties of each sorbate\textsuperscript{28-31}.

<table>
<thead>
<tr>
<th></th>
<th>CO\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
<th>O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_C) (K)</td>
<td>304.128</td>
<td>126.192</td>
<td>154.581</td>
</tr>
<tr>
<td>Kinetic Diameter (Å)</td>
<td>3.3</td>
<td>3.64</td>
<td>3.46</td>
</tr>
<tr>
<td>Quadrupole Moment 10\textsuperscript{40} (cm\textsuperscript{2})</td>
<td>13.4</td>
<td>4.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Polarizability (Å\textsuperscript{3})</td>
<td>2.65</td>
<td>1.76</td>
<td>1.60</td>
</tr>
<tr>
<td>(\varepsilon) (K)</td>
<td>C: 27, O: 79, N: 36, COM: 0</td>
<td>O: 49, COM: 0</td>
<td>0</td>
</tr>
<tr>
<td>(\sigma) (Å)</td>
<td>2.8</td>
<td>3.05</td>
<td>3.31</td>
</tr>
<tr>
<td>(q) (eV)</td>
<td>0.7</td>
<td>-0.35</td>
<td>-0.482</td>
</tr>
</tbody>
</table>

GCMC adsorption simulations are performed using MCCCCS Towhee\textsuperscript{32} with chemical potentials for polar gases calculated from NPT simulations also run using MCCCCS Towhee and for CH\textsubscript{4} from the ideal gas approximation used previously\textsuperscript{33}. Given the rigid and complex polymer structure, MC moves have vanishingly small probabilities to successfully move the polymer, thus the polymer is treated as fixed and rigid during
the adsorption simulations. Total adsorption uptake from simulations is converted to excess adsorption for easier comparison to currently available and potential future experimental data according to Eq. 5.1:

\[ n_{\text{exc}} = n_{\text{tot}} - v_{\text{pore}} \rho_g \]  

(5.1)

where \( n_{\text{exc}} \) is the excess amount adsorbed, \( n_{\text{tot}} \) is the total amount adsorbed, \( v_{\text{pore}} \) is the pore volume and \( \rho_g \) is the gas density from equations of state via the NIST Webbook\(^{31}\). All adsorption isotherms are averaged over five unique samples.

5.2.2 Structure Generation

As this work uses molecular simulations to study the physical properties of PIMs, a realistic polymer model is the foundation for high quality and reliable results. The structure generation techniques are the same as in previous chapters. Polymer chains are randomly initiated throughout the simulation box and grown in a stepwise manner by randomly choosing one of the two chiralities and one of the two possible orientations, until the target chain length is achieved or an overlap results from any further growth. Ultimately, the growth stage is completed when a target density is achieved. The system is grown at a low density, approximately 0.07 g cm\(^{-3}\), to avoid hard core overlaps. The initial growth stage is followed by a molecular dynamics (MD) compression and relaxation scheme, outlined in Table 3.2, in which the pressure is ramped up and then back down in a series of alternating short NVT and NPT runs. The compression and relaxation scheme brings the system to realistic densities; in the case of PIM-1, densities are comparable to reported experimental values. In both simulations and experiments,
density is measured with the same mass, but different volumes. It is convenient in simulations to take the volume as the total volume of the sample while experimentally one considers the skeletal volume. Helium adsorption simulations are used to find the pore volume which is then used to calculate the skeletal density from the simulated density for comparison to experimentally measured densities\textsuperscript{33}.

### 5.3 Results and Discussion

As in previous work, GCMC simulations are used to calculate the gas adsorption capacity of each polymer. Here we focus on the industrially relevant gases CO\(_2\), N\(_2\), and O\(_2\). These gases are of interest not only due to their industrial significance, but also their electrostatic structure and linear shape, which will increase our understanding of the gas-polymer interactions and the importance of the electronic structure of the polymer matrix itself.

Simulated CO\(_2\) adsorption as a function of pressure at 20 C for PIM-1, PIM-1c, PIM-1n, and PIM-1f are compared to experimental CO\(_2\) adsorption at 20 C in PIM-1 in Figure 5.2. As PIM-1 films have been observed to swell under CO\(_2\) adsorption\textsuperscript{34}, this is likely the cause of the hysteresis seen in the experimental data. Experimental data points represent pseudo equilibrium values taken after several hours of equilibration once the differential mass uptake has become sufficiently small. The stiff and rigid polymer backbones make relaxations, and therefore complete equilibration, particularly slow. True equilibrium adsorption values likely lie between the hysteresis loops, and given
sufficiently long equilibration times, the hysteresis is expected to disappear. As MC simulations are not well suited to simulate PIM motions, the polymer is assumed, in this work, as fixed and rigid and therefore prevents any swelling. Future work, exploring hybrid MC/MD to model adsorption induced swelling, is expected to more accurately reproduce the experimentally observed positive linear slope at higher pressures.

Figure 5.2: Figure 1: CO₂ adsorption as a function of pressure in PIM-1 (●), PIM-1c (■), PIM-1n (♦) and PIM-1f (▲) compared to experimental data for PIM-1 (+) 35, all at 20 C. All simulations show an asymptotic approach to a maximum capacity while the experimental data moves towards a constant slope. This is likely due to the model assumptions of a fixed and rigid framework as compared to the experimentally observed swelling.
Regardless of the fixed framework assumption, the simulations of CO$_2$ in PIM-1 give good quantitative agreement with experimental data. Comparing the simulated adsorption isotherms one can start to understand the effect of the structural changes. The PSDs from Figure 4.4 show PIM-1c to have the smallest average pore size, which maximizes gas-polymer interactions causing high uptake at low pressures, and Table 4.2 shows that it has the smallest pore volume, which acts to limit the maximum uptake capacity, all of which is consistent with the adsorption isotherms in Figure 5.2. Given the large surface area and comparable pore volume, the poor performance of PIM-1f is surprising. It should be noted that while PIM-1f shows a lower uptake than the other polymers over the pressure range studied here, it appears to be converging to a similar maximum capacity. By replotting the adsorption data on a volumetric (mmol/cm$^3$) rather than gravimetric (mmol/g) basis in Figure 5.3, the high density of PIM-1f is disregarded and it shows greater quantitative agreement with the other polymers. It is possible that the electronic structure of the CF$_3$ groups act to inhibit the adsorption of polar gases with its negatively charged surface, inhibiting adsorption at low pressures, but at sufficiently large pressures, the pores manage to fill. Conversely, in the other PIMs, the various functional groups, the aromatic nitrogen, nitrile, and carbonyl groups create local quadrupole or dipole moments that may interact favorably with CO$_2$, N$_2$, and O$_2$. 
The electrostatic interaction between the polymer and the gas as well as the gas with itself are important. For PIM-1, the electrostatic interactions were modified to study the importance of the charges. In Figure 5.4, CO$_2$ adsorption as a function of pressure for PIM-1 samples with different charges are compared. Samples with charges from \textit{ab initio} calculations, as in Figure 5.3, are compared with samples in which the charges of the polymer are set to zero, and with all Coulombic interactions turned off. All charge modifications were applied after the structure was created, that is, each of the five samples structures were subjected to the 21 step slow decompression with \textit{ab initio} charges such that the polymer conformation is identical in all three cases. The charges on

Figure 5.3: Simulated data from Figure 5.2 replotted on a volumetric basis (mmol/cm$^3$) for PIM-1 (○), PIM-1c (■), PIM-1n (♦) and PIM-1f (▲). Here, the higher density PIM-1c and PIM-1f systems improve performance relative to PIM-1 and PIM-1n.
the polymer increase the adsorption of CO$_2$. When all electrostatic interactions are turned off, CO$_2$ uptake decreases again over the entire pressure range. At higher pressures, it is reasonable to assume some degree of multilayer coverage which suggests that the electrostatic contribution to the adsorbed phase acting as adsorption sites is significant.

![Graph](image)

**Figure 5.4:** The effect of electrostatic interaction and polymer charge on CO$_2$ adsorption is compared at 20 C. Uptake decreases as charges are adjusted from *ab initio* calculations (●), to polymer partial charges of zero (■), and no Coulombic interactions (♦). Experimental data (+) from Figure 5.2 is plotted for comparison.

Similar trends for O$_2$ and N$_2$ adsorption are observed between the different polymers in Figure 5.5. Continuing to follow gas condensability, O$_2$ shows a greater adsorption capacity than N$_2$ by a small degree. The polymers compare to one another similarly to CO$_2$ at low pressures. That is, PIM-1c and PIM-1n show a greater uptake than PIM-1, and PIM-1f with its large density performs poorly in the gravimetric
comparison. In the case of O$_2$ and N$_2$, the amount adsorbed is significantly lower than the case of CO$_2$, thus the pores do not approach capacity so the low pore volume and pore size PIM-1c do not act to limit adsorption over this temperature and pressure range. Due to the low total uptake, reploting the adsorption capacity volumetrically has a minimally observable effect.
Figure 5.5: (a) N\textsubscript{2} and (b) O\textsubscript{2} adsorption as a function of pressure at 20 C in PIM-1 (●), PIM-1c (■), PIM-1n (♦), and PIM-1f (▲) are compared.
5.4 Conclusions

In all cases, the adsorption capacity of the PIMs studied here was greatest from CO$_2$ > CH$_4$ > O$_2$ > N$_2$, following from gas condensabilities. CO$_2$ has the strongest quadrupole moment and strongly interacts with itself, which, combined with its small kinetic diameter and low critical temperature, make it unsurprising that it is absorbed in the highest amount in all polymers. The generally weaker adsorption of all gases by PIM-1f seen in the plots is due in part to the gravimetric measure used. When adsorption per unit volume, rather than per unit mass (mmol/cm$^3$ rather than mmol/g), is plotted, the higher density PIM-1c and PIM-1f show improved uptake relative to PIM-1 and PIM-1n. Combined with the results from the previous chapter, we can conclude the basic design principles: 1) chain spacing can be influenced by spirocenter functionalization and backbone rigidity, 2) the effect of any functional modification on pore filling should be considered, 3) the electronic structure should be designed to create local dipoles and quadrupoles in order to maximize interactions with polar gases, and 4) system density influences storage density meaning creative use of lightweight constituent elements in monomer design is important in meeting particular gravimetric or volumetric storage targets.

5.5 Bibliography

Chapter 6

Synopsis

The last several chapters have presented the results of research efforts using experiments and simulations to understand the complex materials properties and relationships in PIMs. Experimentally, CO₂ and CH₄ isotherms were measured at multiple temperatures allowing for the calculation of various materials properties. Then, simulations of PIM-1 and its functional variations allowed for enhanced understanding of experimental data, materials properties, and some insight into generalizable design principles for future PIMs.

Due to the minimal amount of existing experimental data, CO₂ and CH₄ adsorption isotherms were measured in PIM-1 at three temperatures. The experiments used a gravimetric balance with buoyancy correction to give high quality data that is in agreement with that published elsewhere. Adsorption isotherms were used to calculate selectivities, enthalpies of adsorption, and diffusion coefficients. Analysis of the adsorption kinetics suggested swelling, even in the powdered sample used. Given the baseline data, work shifted focus to simulations.

A method to create realistic simulation samples was developed and validated for PIM-1. The simulated cubic sample required a box length of at least 40 Å. The resulting samples give experimentally realistic densities with isotherms that qualitatively and quantitatively reproduce experimental data. The geometrically measured pore size distribution suggests that PIM-1 has a unimodal distribution with a long tail. The
simulated PSD peak is at a smaller pore size than that observed by nitrogen adsorption, and does not have a second mode as suggested by PALS, though the first PALS peak is at a similar pore size as the simulations. Given the good agreement between simulated and experimental density and adsorption isotherms, the simulations were extended to three functional variations of PIM-1.

In chapter 4, simulated methane adsorption in PIM-1c, PIM-1n, and PIM-1f were conducted. PIM-1c, PIM-1n, and PIM-1f are modifications to the functionality along the backbone, at the spirocenter, and at both locations, respectively, of PIM-1. Shifts in the PSD peaks were observed to be commensurate with spirocenter functional group volumes for both PIM-1c and PIM-1n, while PIM-1f showed the increase in interchain spirocenter spacing, but lacked the corresponding change in PSD. This failure to increase pore size in PIM-1f may be due in part to pore filling by the large functional groups along the polymer backbone. Simulated scattering in PIM-1 showed the characteristic peaks observed in experimental WAXS data. The scattering patterns of PIM-1c and PIM-1n were similar to that of PIM-1, while PIM-1f was missing the high q peak, likely due to changes in backbone functionality. Adsorption isotherms of the four polymers were in general similar. PIM-1n, with its low density showed the highest adsorption capacity when measured gravimetrically. PIM-1c and PIM-1f, with their high densities, performed poorly when data is considered gravimetrically. When considered on a volumetric basis, PIM-1c showed the highest uptake and PIM-1f became more comparable to PIM-1 and PIM-1n.

In chapter 5, the simulations were extended to investigate the industrially relevant gases of CO₂, O₂, and N₂ in all four polymer structures. The experimental CO₂
adsorption isotherm shows a hysteresis loop and positive limiting slope suggesting that polymer swelling is an important factor. MC methods cannot sufficiently model the motion of PIMs while MD methods cannot effectively model fluctuations in the number of particles. As adsorption is modeled using GCMC, the framework is assumed as fixed and rigid likely contributes to the distinctly different shape of the sorption isotherms. As was noted for methane adsorption, the polymer density was important in determining polymer performance on a per unit mass and per unit volume basis. Gravimetrically, the high density PIM-1c and PIM-1f samples perform relatively poorly compared to PIM-1 and PIM-1n. However, on a volumetric basis, PIM-1c performs very well and PIM-1f is comparable to the others. For N\textsubscript{2} and O\textsubscript{2} adsorption isotherms, PIM-1, PIM-1c, and PIM-1n show nearly identical uptakes while PIM-1f has very low capacity for both. In all cases, adsorption capacity from greatest to least is CO\textsubscript{2} > CH\textsubscript{4} > O\textsubscript{2} > N\textsubscript{2}.

The work to date suggests several basic design principles: 1) chain spacing can be influenced by spirocenter functionalization and backbone rigidity, 2) the effect of any functional modification on pore filling should be considered, 3) the electronic structure should be designed to create local dipoles and quadrupoles in order to maximize interactions with polar gasses, and 4) system density influences storage density meaning creative use of lightweight constituent elements in monomer design is important in meeting particular gravimetric or volumetric storage targets.
6.1 Future Work

The work conducted to date has provided valuable insight into understanding the complex connections between polymer chemistry, morphology, and gas interaction. Future work may look to advance in several key directions: gas dynamics, polymer dynamics, and monomer structure. The following sections will discuss each of these three directions in further detail.

6.1.1 Gas Dynamics

The dynamics of the gas during and after the adsorption process is important to understand. Of primary concern is the diffusion coefficient. Porous materials used in separations technology can rely on several means to effectively separate a gas. Diffusion selectivity, defined as $D_a/D_b$, combined with solubility selectivity, $S_a/S_b$, give the overall permiselectivity, $P_a/P_b = D_a/D_b \times S_a/S_b$. Simulations determining the diffusion coefficient will be useful in understanding the basis of a material’s selectivity and in designing and screening new materials.

Self-diffusion coefficients of a gas in amorphous materials can easily be measured by MD. It is important to note that MD simulations based on equilibrium starting conditions will give the self (tracer) diffusion coefficient, which is different than the typical experimental steady state values. In an MD simulation, the diffusion coefficient can be calculated by the Green-Kubo relation from particle velocities, or from the Einstein relation according to the mean squared displacement $^2$. The Green-Kubo formulation is hindered by the short time dominance and long time noise in the velocity
autocorrelation function. This generally makes the Einstein method the preferred choice. The Einstein relation:

$$6Dt = \langle |R_i(t) - R_i(0)|^2 \rangle$$ \hfill (6.1)

states that the mean square displacement of a particle is proportional to time. The mean square displacement, the ensemble average of which is taken for all gas particles in the system, is plotted against time such that the diffusion coefficient can be calculated from the limiting slope (after the hydrodynamic limit has been achieved). A thorough overview of computational approaches to permeation in polymers is given elsewhere $^3, 4$.

In addition to diffusion, insight into adsorption sites will be of interest. Further study into variations on both backbone chemistry and polymer functionality on strength of interaction with the gas are necessary, of particular interest will be the enthalpy of adsorption. The enthalpy of adsorption is tricky to measure experimentally, requiring the measurement of several isotherms at varying temperature and the application of the Clausius-Clapeyron equation as in Chapter 2. From simulations, the enthalpy of adsorption (or isosteric heat of adsorption) can be measured by$^5$:

$$-\Delta H^\circ = Q_{st} = RT \left( \frac{\langle E_{tot}^\circ N \rangle - \langle E_{tot}^s \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + \frac{\langle E_{tot}^g N \rangle - \langle E_{tot}^g \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \right)$$ \hfill (6.2)

where $R$ is the gas constant, $T$ is the temperature, $E$ is the energy in the adsorbed and gas phases, and $N$ is the number of particles adsorbed. For an ideal gas, the third term for the gas state goes to zero, while for non-ideal gases, another simulation must be run to calculate the gas phase energies. Theoretical work on optimal enthalpies of adsorption for various storage applications have been conducted and provide interesting design criteria for porous materials$^6$. Similar theoretical calculations for inhomogenous and
complex pore topologies could be investigated and return interesting insights testable by simulations.

6.1.2 Polymer Dynamics

Experimental evidence suggests that PIM-1 membranes swell on the adsorption of various gases (1.94% for CH$_4$ and 7.75% for CO$_2$ via integral sorption at 10 bar$^\dagger$). The challenge in modeling this phenomenon arises from the nature of MD and MC simulations. MD simulations are well suited to the motions of polymer chains, particularly PIM chains, even at high densities, but do not have a well developed ensemble in which particles can be added to the simulation. Conversely, MC simulations, which can use the grand canonical ensemble to study adsorption and fluctuate the number of particles in the system, fail to adequately move and relax highly connected and dense polymer systems like PIMs.

Hoelck$^{1,7}$ modeled this phenomenon with “pre-swollen” packing models, in which the framework density was reduced by various means to simulate the swollen state. Unfortunately, a pre-swollen model only accurately describes the system at a single temperature and pressure such that the model poorly reproduces adsorption isotherms at any other pressure. Several alternative schemes could be investigated, namely hybridizing the MC and MD simulations. Tenney$^8$ showed that alternating between MC and MD steps with a script that connected DL_POLY and MCCCS Towhee is possible. His findings suggest that a more streamlined technique is required, allowing for further investigation of the effects of the ratio and number of MD and MC steps in each cycle.
6.1.3 Monomer Structure

In the work presented here, the primary focus has been on understanding the polymer and its interactions with various gases in order to design PIMs with better performance characteristics. So the question remains, how does one make a PIM with the highest adsorption capacity, permeability, and selectivity?

Early work suffered from a typo that set the torsional parameters to a value two times that suggested by the force field. PSDs, SAs, and adsorption capacities of these overly stiff materials were very high. Details are presented in Appendix B. Adsorption isotherms overestimated experimental values by roughly 40% and surface areas were higher than current simulations by a factor of two. This suggests that future work should focus on methods to further enhance polymer rigidity.

How to increase the stiffness of fused aromatic rings is a challenge to chemistry. The PIM-1 synthesis results in the inclusion of flexible oxygen atoms in the polymer backbone. If a means to replace these oxygen atoms with something more rigid such as carbon or nitrogen could be achieved, polymer stiffness and associated properties would be expected to improve. Considering other porous materials (hypercrosslinked polymers, diamondoid structures, MOFs, COFs, etc.) as well as the experimentally synthesized and characterized PIMs, networking seems to be one means to achieve high surface areas. In attempt to maintain the solubility and processability of PIM-1 like materials, perhaps post synthetic or post film casting crosslinking methods should be considered.

One of the great advantages of polymers is functionalization, the ability to incorporate a chemical species of interest to the monomer. The exploration of functional
group variation to PIM-1 through simulations will continue to be of interest. It is tempting to try drastic or extreme variations, but stepwise functional changes allow for easier connection between observed macroscopic property, and microscopic changes. A faster and simpler means to create PIM structures will be useful in allowing more functional varieties to be tested more easily allowing the researcher to build up to a more drastic change. With respect to the functionality added, the effect of increased gas-polymer interaction and interchain separation must be weighed against possible pore filling. Finally, implementation of simulated measurement of the enthalpy of adsorption will be critical to determining the effectiveness of a functional group and the potential of the material for various practical applications.

6.2 Conclusions

Polymers of intrinsic microporosity represent a novel class of polymers with many interesting and potentially fruitful applications. Shown by the number of related publications, PIMs have captured the interest of many. The simplicity in design – rigid and non linear – combined with the variety in monomer chemistry make the future of PIMs full of opportunity. The work presented here is far from complete. Possibilities for improvement abound as do directions for future work. As much as anything, this work has shown the potential utility of simulations for the understanding and exploration of PIMs and laid a foundation from which more interesting questions can be investigated.
6.3 Bibliography

Appendix A

Simulation Details, Codes and Scripts:

This chapter provides further details on the simulations. Due to space limitations, the actual structure generation code is not printed below but will be available upon request. The appendix is organized as follows: in section A.1, the simulation parameters (bonded and nonbonded) are listed in a consolidated format (references are as previously cited), in section A.2 the LAMMPS input script implementing the 21 step compression and relaxation (as well as RDF calculation and trajectories for simulated scattering) are given, and in section A.3 an example MCCCS Towhee script for the simulated adsorption of CO$_2$ is given.

A.1 Structure Generation Code

The FORTRAN 90 code written for this work to create a sample of PIM-1 is available upon request. The user must compile this code using a standard fortran compiler, this code has only been tested on the intel fortran and GNU fortran compilers. Comments have been added throughout the code in attempt to improve clarity and readability for the author. The user must supply a "monomer" file which is a modified xyz file containing the total number of atoms on line 1, a comment on line 2, and in columns 1, 2, 3, 4, 5, and 6 of the rest of the file, the element type, atom type, charge, and x, y, and z coordinates, respectively (the file for PIM-1 is supplied after the code)
describing the monomer shown in Figure 3.1. This code outputs xyz files showing
wrapped and unwrapped coordinates, as well as a LAMMPS data file to be used for MD
or MC simulations (MCCCS Towhee can read in a LAMMPS data file). This code may
be modified to create the other functional variations of PIM-1 by substituting the correct
bonded and nonbonded parameters from the following tables and updating the
connectivity in the LAMMPS output section.
### Table A1: Simulation Parameters for PIM-1, PIM-1c, PIM-1n, and PIM-1f

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<th>$\sigma$ (Å)</th>
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<th>PIM-1c</th>
<th>PIM-1n</th>
<th>PIM-1f</th>
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<td>Charge (eV)</td>
<td>Number</td>
<td>Charge (eV)</td>
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<td>36, 37</td>
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Table A2: GAFF atom names and description used for simulations of PIMs

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<tr>
<th>GAFF Name</th>
<th>GAFF Description</th>
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<tbody>
<tr>
<td>ca</td>
<td>Sp2 C in pure aromatic systems</td>
</tr>
<tr>
<td>c3</td>
<td>Sp3 C</td>
</tr>
<tr>
<td>os</td>
<td>Ether and ester oxygen</td>
</tr>
<tr>
<td>c1</td>
<td>Sp C</td>
</tr>
<tr>
<td>n1</td>
<td>Sp N</td>
</tr>
<tr>
<td>c2</td>
<td>Sp2 C</td>
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<td>o</td>
<td>Oxygen with one connected atom</td>
</tr>
<tr>
<td>nc</td>
<td>Sp2 N in non-pure aromatic systems</td>
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<tr>
<td>f</td>
<td>Fluorine</td>
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<tr>
<td>cg</td>
<td>Inner Sp carbons in conjugated systems</td>
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Table A3: Bond, angle, and torsion parameters from the GAFF used in this work. White corresponds to PIM-1 or common to all PIMs studied here, green to PIM-1c, orange to PIM-1n, and purple to PIM-1c.

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<td>ca-ca</td>
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<td>1.373</td>
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<tr>
<td>c1 - ca</td>
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<td>c3 - f</td>
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<table>
<thead>
<tr>
<th>Angle</th>
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<th>$\gamma$ ($^\circ$)</th>
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</table>
A.2 Compression

The following code is a LAMMPS input script used to implement the 21 step compression scheme. Note that as LAMMPS continues development, some nomenclature may need to be updated, in particular, newer versions of LAMMPS may require a minor update to the “fix nvt” and “fix npt” calls in this script; this script was used with the 15 February 2010 version of LAMMPS. Comments have been added to aid the author during script development. The last stage of this simulation calculates trajectories for use in simulated scattering and also collects (and averages) radial distribution functions for atom type 11 (the spirocenter carbon). Further information about any commands may be found in the LAMMPS documentation.

# PIM-1 compression

#################
# Initialization:
#################
units real          # see http://lammps.sandia.gov/doc/units.html for units
# dist = angstrom, time = femtoseconds, energy = Kcal/mole
atom_style full     # (molecular + charge): atom-ID molecule-ID atom-type q x y z
# check atom_modify command for further options (array vs. hash, etc)
dimension 3         # default value
newton on           # default value: save computations at cost of communication
# processors Px Py Pz: "this command should be used to override the LAMMPS
# default if it is known to be sub-optimal for a particular problem."
boundary p p p      # default value, periodic in x, y, and z

pair_style lj/cut/coul/long 15.0          # cut LJ and Coul at 15.0 A
# see dielectric command
kspace_style ewald 1.0e-4                # ewald + precision

pair_modify shift yes mix arithmetic     # for use with minimization - avoids discontinuities
# mix arithmetic = lorentz-berthelot mixing rules
bond_style harmonic                      # as used in gaff
special_bonds amber                      # set weighting coeffs for atoms bonded directly or indirectly
angle_style harmonic                      # as used in gaff
dihedral_style charmm                    # single term of AMBER (see notes on special_bonds)

#################
# Atom Definition:
read_data data.pim1

###########
# Settings:
###########
dielectric 1.0  # default value. used to reduce strength of interactions.
neighbor 2.0 bin  # default values of skin and style. used to chang neighbor list modifications.
                 # skin = distance beyond cutoff distance to look, style is method of building
neigh_modify every 1 delay 10 check yes  # mostly default values; "check yes" is key

###########
# Outputs:
###########
thermo_style custom step etotal pe temp press vol evdwl ecout ebond eangle edihed
thermo 500  # output thermo quantities every 500 steps
dump 1 all xyz 1000 pim1.dump.xyz
restart 100000 restart.*

###########
# Run:
###########
min_style sd  # default, conjugate gradient as opposed to steepest decent (sd)
minimize 1.0e-2 1e-2 1000 100000  # recomend using pair_style that goes to 0 at cutoff (change later)
timestep 1.0  # default value for units = real
run_style verlet  # default. can choose respa.
pair_modify shift no mix arithmetic # turn shift off after energy minimization

#1
fix 1 all nvt 600 600 100
velocity all create 600 58447419
run 50000
unfix 1

#2
fix 1 all nvt 300 300 100
run 50000
unfix 1

#3
fix 1 all npt 300 300 100 xyz 1000 1000 100
run 50000
unfix 1

#4
fix 1 all nvt 600 600 100
run 50000
unfix 1

#5
fix 1 all nvt 300 300 100
run 100000
unfix 1

#6
fix 1 all npt 300 300 100 xyz 30000 30000 100
run 50000
unfix 1

#7
fix 1 all nvt 600 600 100
run 50000
unfix 1

#8
fix 1 all nvt 300 300 100
run 100000
unfix 1

#9 Maximum pressure of 50,000 bar
fix 1 all npt 300 300 100 xyz 50000 50000 100
run 50000
unfix 1

#10
fix 1 all nvt 600 600 100
run 5000
unfix 1

#11
fix 1 all nvt 300 300 100
run 10000
unfix 1

#12 Slow decompression of 0.5*Pmax
fix 1 all npt 300 300 100 xyz 25000 25000 100
run 5000
unfix 1
#13
fix 1 all nvt 600 600 100
run 5000
unfix 1

#14
fix 1 all nvt 300 300 100
run 10000
unfix 1

#15 Slow decompression of 0.1*Pmax
fix 1 all npt 300 300 100 xyz 5000 5000 100
run 5000
unfix 1

#16
fix 1 all nvt 600 600 100
run 5000
unfix 1

#17
fix 1 all nvt 300 300 100
velocity all create 300 58447419
run 10000
unfix 1

#18 Slow decompression of 0.01*Pmax
fix 1 all npt 300 300 100 xyz 500 500 100
run 5000
unfix 1

#19
fix 1 all nvt 600 600 100
run 5000
unfix 1

#20
fix 1 all nvt 300 300 100
run 10000
unfix 1
A.3 MCCCS Towhee Adsorption

In this section, the input script to perform GCMC using MCCCS Towhee is given. After running the LAMMPS compression, use the restart2data script (included with LAMMPS) to create a LAMMPS data file from a restart file. Reorder the atoms in ascending order and run Towhee with an input format of “LAMMPS” to import the structure and connectivity to Towhee as described in the software documentation; failure to do so will create errors when Towhee is used for the adsorption simulations. The following is the input script for the adsorption of CO$_2$ into a polymer framework:

```
inputformat  'Towhee'
randomseed  1302002
random_luxlevel  3
random_allow_restart  T
ensemble  'uvt'
temperature  293.15d0
```
nmolty
12
nmolectyp
1 1 1 1 1 1 1 1 1 1 500
chempot
0 0 0 0 0 0 0 0 0
numboxes
1
stepstyle
'moves'
nstep
30000000
printfreq
1500000
blocksize
1500000
moviefreq
1500000
backupfreq
1500000
restartfreq
0
runoutput
'blocks'
pdb_output_freq
3000000
loutdft
F
loutlammmps
T
loutdipoly
F
pressurerefreq
0
trmaxdispfreq
100
volmaxdispfreq
0
potentialstyle
'internal'
ffnumber
2
ff_filename
towhee_ff_pim1
/gpfs/work/gsl130/bin/towhee-6.2.12/ForceFields/towhee_ff_TraPPE-EH
#/home/greg/towhee-6.2.12/ForceFields/towhee_ff_TraPPE-EH
classical_potential
'Lennard-Jones'
classical_mixrule
'Lorentz-Berthelot'
lshift
F
F
rmin
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rcut
  15.00000000000000
rcutin
  10.00000000000000
electrostatic_form
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coulombstyle
  'ewald_fixed_kmax'
kappa
  5.6
kmax
  5
dielectric
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max_bond_length
  4.0d0
nfield
  0
solvation_style
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limit
  .false.
initboxtype
  'dimensions'
initstyle
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inix iniy iniz
  3 3 3
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  0.0000000000000000  43.094556742161146  0.0000000000000000
  0.0000000000000000  0.0000000000000000  43.094556742161146
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  0.330d0
  pmuvctbmt
  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  1.0d0
pmtracm
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  pmtcmt
  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  0.0d0  1.0d0
rmtrac
  1.0d0
tatrac
0.5d0
pmrotate
1.0d0

pmromt
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rromt
1.0d0
tarot
0.5d0
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nch_tor
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nch_bend_a
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nch_bend_b
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bond_sdev_multiplier
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nch_vib
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'analytic Boltzmann using angles'
three_bond_fixed_endpoint_bias_style
'analytic using max and min 2-4 distance'
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'explicit'
...explicit declaration of atom connectivity for each molecule from towhee_alt_inp...
#Carbon Dioxide
input_style
'basic connectivity map'
nunit
3
nmaxcbmc
3
lpdbnames
F
forcefield
'TraPPE-EH'
charge_assignment
'bond increment'
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1  'C_co2'  0.70
vibration
2
2 3
improper torsion
0
unit ntype
2  'O_co2' -0.35
vibration
1
1
improper torsion
0
unit ntype
3  'O_co2' -0.35
vibration
1
1
improper torsion
0
Appendix B

Increased Backbone Rigidity

During the course of this research, a limited number of simulations were conducted in which the torsion parameters were set to a factor of 2 higher than designated by the forcefield. While these results do not accurately model the experimental systems, given the good agreement that simulations obtained with the correct torsional parameters, these results shed light on a path towards improved performance. As a general discussion of the simulation techniques has been presented previously, only a discussion of the results are given here. This work was conducted before the development of PIM-1f, thus results for only PIM-1, PIM-1c, and PIM-1n are presented.

An increase in backbone stiffness enhances the mechanism by which porosity is developed in that efficient packing is further frustrated. Table B1 summarizes the effect of artificially increasing the backbone stiffness on surface area, pore volume, and density in the three polymers studied here. The solvent accessible surface areas effectively double for each polymer. The change in pore volume balances with the change in simulation density leaving the experimental densities nearly identical.
Considering next the effect of backbone rigidity on pore size distribution (PSD),

the PSD for PIM-1 is shown in Figure B1 as a representative example with similar

changes seen in PIM-1c and PIM-1n. The average pore size increases by about an

Angstrom. Possibly of greater importance than the shift in average pore size is the fact

that more large pores are observed. Not only is the maximum pore size observed much

larger, but there are a greater proportion of pores in the 5 to 10 Å range.

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<td>448.986 +/- 85.1830</td>
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<td>Avg. Pore Vol. (cm³/g)</td>
<td>0.347 +/- 0.00652</td>
<td>0.194 +/- 0.01643</td>
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<tr>
<td>Sim. Density (g/cm³)</td>
<td>0.857 +/- 0.02404</td>
<td>0.975 +/- 0.01537</td>
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<td>Exp. Density (g/cm³)</td>
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<tr>
<td>Avg. SA (m²/g)</td>
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<td>319.28 +/- 116.63</td>
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<tr>
<td>Avg. Pore Vol. (cm³/g)</td>
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<td>0.226 +/- 0.143</td>
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<td>Sim. Density (g/cm³)</td>
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<td>1.086 +/- 0.0322</td>
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<td>Exp. Density (g/cm³)</td>
<td>1.345 +/- 0.0199</td>
<td>1.481 +/- 0.320</td>
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<tr>
<td>Avg. SA (m²/g)</td>
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<td>479.73 +/- 98.468</td>
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<tr>
<td>Avg. Pore Vol. (cm³/g)</td>
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<td>0.220 +/- 0.0263</td>
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<tr>
<td>Sim. Density (g/cm³)</td>
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<td>0.959 +/- 0.0209</td>
</tr>
<tr>
<td>Exp. Density (g/cm³)</td>
<td>1.217 +/- 0.0108</td>
<td>1.216 +/- 0.0084</td>
</tr>
</tbody>
</table>

Table B1: Comparison of surface areas, pore volumes, and densities between overly rigid and realistic samples.
The adsorption capacity of the polymers greatly increases with increased backbone rigidity. In Figure B2 CO₂ and CH₄ adsorption isotherms for the increased (open symbols) and realistic (solid symbols) torsions are compared. As no CO₂ data have yet been collected for PIM-1c and PIM-1n with increased backbone rigidity, only data for PIM-1 is compared in Figure B2a. In all cases, the polymers with increased backbone rigidity adsorb significantly higher amounts. Having first examined the effect of increasing backbone rigidity on the various polymer parameters, the increased adsorption capacity is not surprising. The larger pore volumes and increased proportion of larger pores allows for greater adsorption capacity.
Figure B2: (a) CO\textsubscript{2} in PIM-1 with regular (●) and increased (○) backbone rigidity and (b) CH\textsubscript{4} adsorption isotherms in PIM-1 (●), PIM-1c (■), and PIM-1n (♦) with the increased (open symbols) and realistic (solid symbols) torsional parameters.
Bhatia and Myers (Langmuir 22 (4), 2006) calculate optimal center to center pore widths for the storage of hydrogen and methane in carbonaceous slit pores as 9.2 and 10.45 Å respectively. Approximating that PIMs form slit pores and that all atom are roughly equal in size to carbon, these calculations can be applied to PIMs. As the PSDs measured in this work are wall to wall, subtracting the carbon diameter of 3.4 Å (used to calculate the optimal pore widths) from the optimal pore widths of Bhatia and Myers gives the optimal pore width for CH$_4$ as roughly 7 Å. This is significantly higher than the average pore size obtained in PIMs when using the realistic torsions. Using the increased torsions, the average pore size increases closer to the optimum pore size and more pores of optimum size are present.

This exploration into backbone rigidity suggests a clear path to improved PIM performance. However, PIMs were already designed to have highly rigid backbones which will make further increases in rigidity difficult. All PIMs studied in this work contain oxygen atoms in the backbone, which due to their increased flexibility compared to the aromatic carbon atoms, offer a potential point of improvement.
VITA

Gregory Steven Larsen

Gregory Larsen was born June 1st, 1984 in St. Paul, Minnesota. In May 2006, Greg graduated with a BS in Physics from Rice University. In January 2007, Greg started his graduate studies in the Materials Science and Engineering department at the Pennsylvania State University. Under guidance from Dr. Coray Colina, his dissertation involved the characterization of polymers of intrinsic microporosity through simulations and experiments.